47th ANNUAL MEETING OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVI APRIL 1951 No. 4

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ERRATA

The following errors have been noted in the paper "Study of the Tannin Contents of Barks from the Florida Scrub Oaks, *Quercus laevis* and *Q. cinerea*", which appeared in the November 1950 Journal.

Page 734, 2d line of next to last paragraph under "Sampling of Bark"—". . . areas in Florida in which scrub oaks occurred" should read ". . . areas in the peninsular part of Florida in which scrub oaks occurred."

Page 735, last word of the third line of text — Should be "black", making the sentence read "Since none of the plots contained blackjack oak, *Q. marilandica* Muenchh, it was omitted from the study."

Page 742, Figure 2-B — Legend should read "Peeled sections from most representative tree on Plot E . . ." rather than "Plot *C*."

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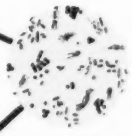

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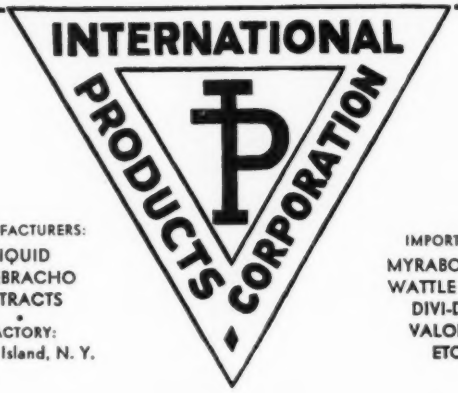

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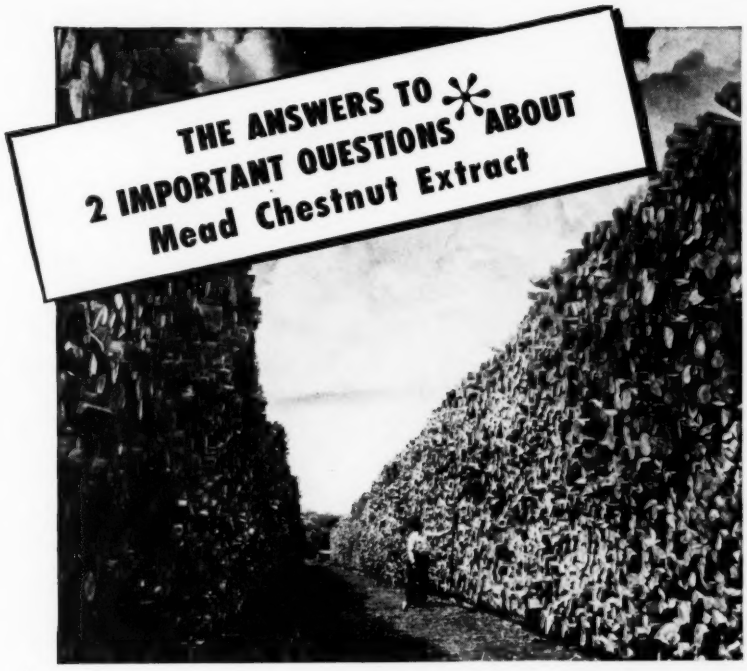

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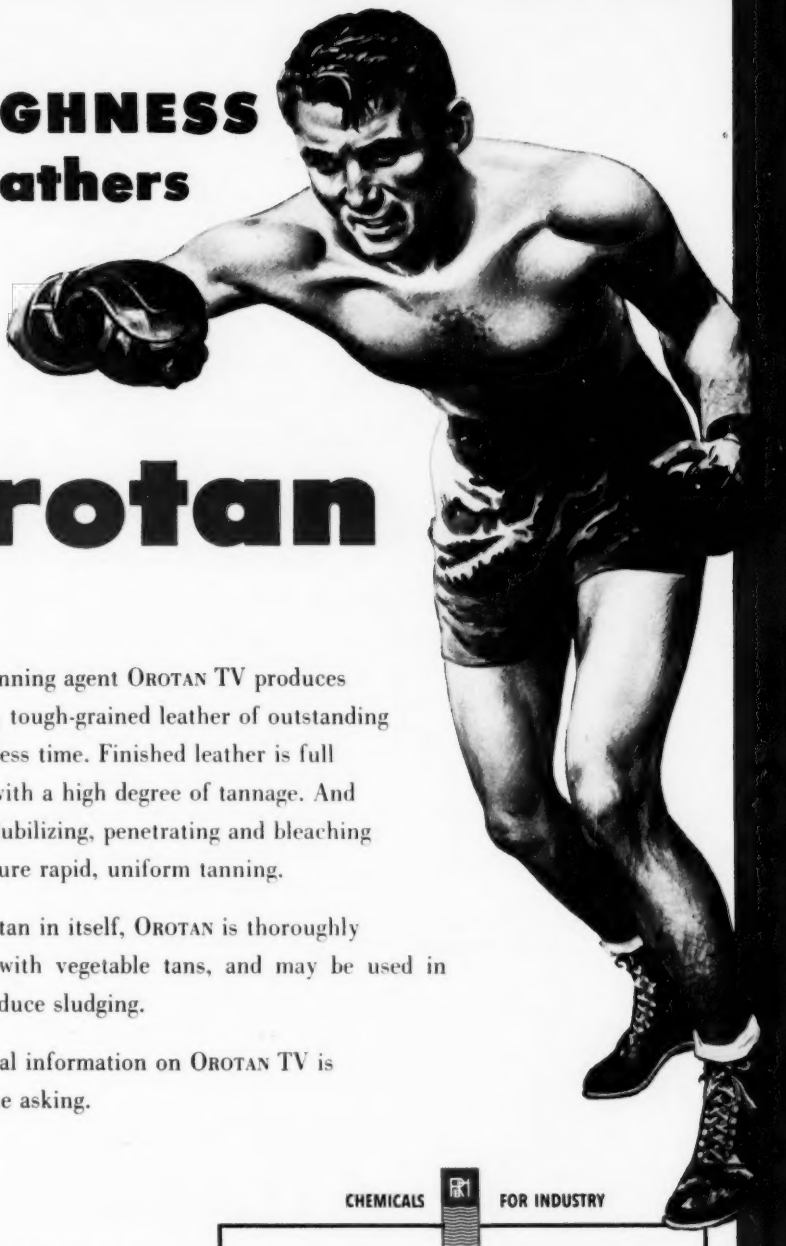

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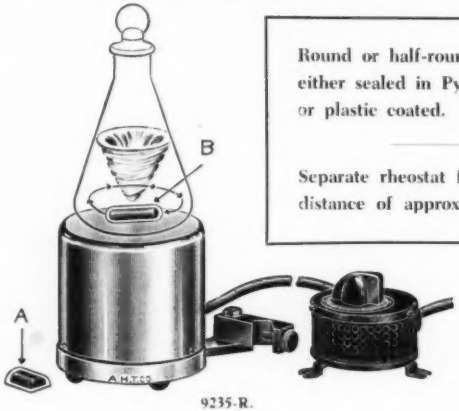

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VOL. XLVI APRIL 1951 No. 4

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PROPOSED AMENDMENT OF BY-LAWS

These proposed amendments of the By-Laws of the Association are as presented to the Council by the By-Laws Committee and revised by Council at its meeting on February 14, 1951. Action on the proposed amendments will be taken in accordance with Article X, Section 3 of the By-Laws, which reads as follows:

"All proposed amendments shall be brought before the Annual Meeting for discussion and vote. It shall be within the province of the members voting to adopt or reject such amendment, or to order that it be returned to Council for further study or revision. Members unable to be present may record their votes for or against such amendments by notifying the Secretary in writing at any time before the amendment is brought to a vote. The total vote cast shall equal at least one quarter the number of the Active membership of the Association at the time the vote is taken. A two-thirds vote of the Active members voting, by ballot, shall be required to adopt an amendment."

As the proposed amendments represent the most important changes in the organization of the Association that have been undertaken in many years, members are urged to take advantage of the privilege of a mail ballot if necessary.

ROBERT B. HOBBS
Chairman, By-Laws Committee

Amendment 1. Article III, Section 2, Paragraph e shall be deleted and replaced by the following:

"Mutual members shall be members in good standing of any foreign association of professional leather scientists, who shall have applied for mutual membership by virtue of a special agreement for reciprocal mutual membership entered into by this Association and the foreign Association, as provided in Article IV."

Amendment 2. The last sentence of Article III, Section 3, Paragraph b shall be amended to read as follows:

"Each application shall be accompanied by the payment of one year's dues, except in the case of any members in good standing making application for a change in classification of membership."

Amendment 3. The first sentence of Article III, Section 3, Paragraph c shall be amended to read, in part, as follows:

"Application for active, associate, or student membership shall be received by the Secretary . . ."

The rest of the sentence shall remain unchanged.

Amendment 4. Article III, Section 3, Paragraph e shall be amended by adding the following sentences:

"A student membership shall be valid for one year only unless renewed. A student member may renew his membership by submitting, with payment of annual dues, a statement that he is still qualified for student membership by virtue of being registered at an accredited institution of learning, as provided in Article III."

Amendment 5. A new paragraph (f) shall be added to Article III, Section 3, to read as follows:

"Any associate member in good standing who becomes eligible for active membership may request that his classification be changed to active member. Any student member in good standing may, upon graduation from any accredited institution of learning, request that his classification be changed to associate member. In neither of the above cases shall formal application be required. Any such request may be approved by majority vote of Council."

Amendment 6. Article IV, Section 1, paragraph (c) shall be amended by changing the clause "and two councilors shall be elected in odd-numbered years" to read, "and three councilors shall be elected in odd-numbered years."

Amendment 7. Article IV, Section 1 shall be amended by adding a new paragraph (g) as follows:

"No Councilor shall be eligible for reelection to a second consecutive full term as Councilor. This shall not preclude the election of a Councilor to the office of President-elect, or the election of a President whose term is about to expire to the office of Councilor."

Amendment 8. Article IV, Section 2, paragraph (b) shall be deleted and replaced by the following:

"The President-elect shall act for the President during the absence or temporary incapacitation of the latter, and shall act as Coordinator of Technical Committee Activity, in which capacity he shall perform the following duties:

(1). To serve as chairman of the Technical Committee Board, and to call at least one meeting of the board during each calendar year to review activities of the Technical Committees.

(2). To define, subject to approval by Council, the scope of Technical Committee assignments.

(3). To recommend or assign new problems to Technical Committees, and to suggest sub-committees for handling such problems.

(4). To assist Chairman of Technical Committees in the selection of members of sub-committees.

(5). To serve as the Technical Committees' representative on the Council and to propose to Council any actions necessary to promote Committee

activity; to arrange, at the request of a Chairman of a Technical Committee, for space on Council's agenda for the presentation of Committee reports and the discussion of special problems of the Committee.

(6). To maintain a current record of the progress of assignments of Technical Committees.

On petition of the President-elect or if for any other reason he is unable to serve, Council shall have power to appoint another of its members as Coordinator of Technical Committee Activities."

Amendment 9. In Article IV, Section 3, paragraph (d), clause (2), the word "methods" shall be changed to "Technical", and "IX" shall be changed to "X".

Amendment 10. Two new clauses shall be added to Article IV, Section 3, paragraph (d), as follows:

"(11) To enter into special agreements with foreign associations of professional leather scientists for reciprocal mutual membership, provided that any such agreement shall be terminable at will by either party to said agreement at the end of any calendar year upon the giving of reasonable notice of such termination.

"(12) To appoint the Nominating Committee, as provided in Article V."

Amendment 11. The last sentence of Article IV, Section 2, paragraph (f) shall be deleted.

Amendment 12. Article V shall be deleted and replaced by the following:

Article V. Elections

(1). *General Provisions*:

The President-elect and Councilors shall be nominated by a Nominating Committee, or by petition, as hereinafter provided, and shall be elected by secret written ballot of the members eligible to vote.

(2). *Nominations*:

(a) The Council shall, before each Annual Meeting of the Association, appoint a Nominating Committee, composed of three active members, to serve for one year. No officer or councilor shall be eligible to serve on this committee, and no member shall serve on two successive Nominating Committees. The composition of the Nominating Committee shall be reported to the membership at the annual meeting, and shall be subject to ratification by the active members there present. The Council shall designate the chairman of the Nominating Committee. Any vacancies in the Nominating Committee shall be filled by appointment by the President.

(b) The Nominating Committee shall select two candidates for each office to be filled at the next annual election. The chairman of the Nominating Committee shall ascertain that these candidates are willing to serve if elected. The names of the candidates shall be reported to the Secretary not later than January 10th, and shall be published in the February issue of the Journal of the Association.

(c) Additional candidates may be nominated by petitions, signed by 15 or more active members. Such petitions shall reach the Secretary not later than April 1st, and shall contain a statement of the willingness of the nominee to serve if elected. No member shall sign more than one petition for each office to be filled.

(3). *Elections*

(a) The Secretary shall prepare a ballot listing all the candidates nominated for each office in alphabetical order. This ballot shall be sent to each voting member at least thirty days before the date of the next annual meeting.

(b) Each member shall vote for one candidate for President-Elect (in even numbered years) and for as many candidates for Councilor as there are vacancies to be filled. Each ballot shall be enclosed in a sealed envelope marked, "Ballot Envelope." The ballot envelope shall bear no signature or other means of identification. The ballot envelopes shall be handed to the Secretary not later than 10:00 A. M. on the second day of the annual meeting, or may be mailed to reach the Secretary not later than the above day and hour. If mailed, the ballot shall be enclosed in an outer envelope, and the outer envelope shall bear the hand-written signature of the member voting.

(c) The Secretary shall check the ballots against the roster of members eligible to vote. He shall remove the outer envelopes and deliver the ballot envelopes, unopened, to the tellers.

(d) The ballots shall be counted during the annual meeting by three or more tellers appointed by the President. The result of the election shall be announced to the membership during the annual meeting. The candidates for President-Elect who receives the greatest number of votes, and that number of candidates for councilor, equal to the number of vacancies to be filled, who receive the greatest number of votes, shall be declared elected.

(e) In case the ballot for any office results in a tie, the voting members present at the annual meeting shall proceed to vote, by written ballot, on the names of the candidates so tied, and the candidate receiving the largest number of votes shall be declared elected.

Amendment 13. Article VI, Section 1 shall be deleted and replaced by the following:

"(1) *Dues*:

(a) Dues shall be assessed against each member, in accordance with his classification as provided in Article III, and in accordance with special agreements between this Association and foreign associations for reciprocal mutual memberships as provided in Article IV.

(b) The dues for active, associate, and student classifications of membership shall be fixed by the Council, subject to approval by the active members at the Annual Meeting. Payment of dues shall entitle each member to all the privileges of his respective classification of membership as provided in Article III.

(c) Life members and honorary members shall be exempt from the payment of dues to this Association.

(d) In addition to the annual dues provided in this section, each member who holds mutual membership in any foreign association as provided in Article III shall pay such additional fee or fees as shall have been agreed upon by this Association and the foreign association or associations in which such member holds mutual membership.

(e) Each member of a foreign association who is a mutual member of this Association, as provided in Article III, shall pay an annual fee fixed by the special agreement between this Association and the foreign association, which fee shall entitle him to the privileges of mutual membership in this Association as provided in Article III. The amounts of the fees provided for in this paragraph and in paragraph (d) shall be recorded in the office of the Secretary and made known to any member on request.

(f) All dues charged to active, associate, and student members shall be payable to the Secretary on or before January first of each year. Dues charged to mutual members shall be paid to the proper officers of the several foreign associations not later than April first of each year.

(g) The Secretary shall, as of April first of each year, exchange lists of members from whom mutual membership dues shall have been collected, with the proper officers of the several foreign associations. Settlement of balances due to or from this Associations, as determined from such lists, shall be made on or before September first of each year.

Amendment 14. Article VI, Section 3 shall be amended by the addition of a new paragraph (d), as follows:

"(d) Any appropriation, except to cover a deficit in the operating expenses of the Association, which requires the expenditure of funds other than income received during the fiscal year in which the proposed expenditure is to be made, shall be submitted by the Council to the Association for approval. Such approval may be made by a majority of the members voting."

Amendment 15. Article VI, Section 4 shall be amended by adding a new paragraph (d) as follows:

"(d) The budget may annually appropriate to the support of the work of any Technical Committee or subcommittee, on request by the Coordinator of Technical Committee Activity, a basic amount not to exceed twenty-five dollars, for incidental expenses of such Technical Committee or subcommittee. The Chairman of the Technical Committee or subcommittee may expend so much of this basic amount as he considers necessary for the work of his subcommittee or Technical Committee, and shall return any unexpended balance to the Secretary at the end of the fiscal year. Supplementary appropriations for the work of a Technical Committee or subcommittee may be made by Council, and shall be disbursed in the manner provided in Section 3 of this Article.

Amendment 16. Article IX, Section 2, shall be amended by deleting paragraphs (a) through (d), by adding a new paragraph (a) as follows:

"(a) The development of methods, and the consideration of all proposals to adopt, change, or discard any method, shall be in the hands of committees known as "Methods Committees," which shall be subcommittees of Technical Committees, as provided by Article X." and by re-lettering paragraphs (e) through (j) to be (b) through (g), respectively.

Amendment 17. Article X shall be re-numbered to be Article XI.

Amendment 18. A new Article X shall be added, as follows:

17. Insert new Article X as follows:

"*Article X. Technical Committees.*

(1). Establishment of Technical Committees

The Council shall have the power to establish and to discharge permanent technical committees. The Coordinator of Technical Committee Activity shall recommend such action when, in his opinion, it becomes desirable, and shall define the field of work of each technical committee, subject to the approval of Council.

(2) Duties of Technical Committees

Each Technical Committee shall, within the field of work defined by the Coordinator of Technical Committee Activity,

perform those duties assigned by the Coordinator including, but not necessarily or exclusively, the following:

(a) To take charge of the development and revision of methods as provided by Article IX.

(b) To conduct studies of technical problems concerned with leather manufacture and processing.

(c) To conduct studies of technical problems concerned with the standardization and specification of leathers and leather processing materials.

(3) Chairman of Technical Committees

(a) There shall be a Chairman of each Technical Committee, who shall be appointed by the President, with the advice of the Coordinator of Technical Committee Activity, and subject to approval by a majority of the Council.

(4) Subcommittees of Technical Committees

(a) A subcommittee of a Technical Committee shall be created as necessary to handle any problem, which shall have been assigned to the Technical Committee by the Coordinator of Technical Committee Activity. The subcommittee shall be nominated by the Chairman of the Technical Committee with the advice of the Coordinator of Technical Committee Activity, and subject to approval by majority vote of Council, and the Chairman of the subcommittee shall be designated by the Chairman of the Technical Committee.

(b) The size of a subcommittee shall be determined by the Chairman of its parent Technical Committee. In nominating members of a subcommittee, the Chairman of the parent Technical Committee shall give adequate representation, as far as practicable, to the tanning industry, to allied industries, and to independent laboratories, concerned with the problem. The Chairman of the Technical Committee may be a member of a subcommittee. An expert who is not a member of the Association may be a member of a subcommittee, but shall have no vote therein. A student member of the Association may be a member of a subcommittee, but shall have no vote therein. When two or more members of a subcommittee shall be representatives of the same company, independent laboratory, or Government agency, they shall be entitled collectively to only one vote in the subcommittee.

(c) The duties of a subcommittee of a Technical Committee shall be such of the duties of the Technical Committee as

apply to any problems that shall have been assigned to it by the Chairman of the Technical Committee.

(d) A subcommittee shall be automatically discharged when all its assignments are finished. An assignment shall be considered finished when Council or the membership of the Association shall have taken final action on a report of the subcommittee so as to dispose of its problem, or, if no action on the report is required, when the report shall have been presented to Council.

(5) Chairman of Subcommittees

(a) The Chairman of a subcommittee shall be designated by the Chairman of the parent Technical Committee.

(b) The Chairman of a subcommittee shall have the following duties:

(1a)To call and preside at meetings of the subcommittee.

(2a)To be responsible for the assignment to subcommittee members of tasks involved in the study of the problems assigned his subcommittee.

(3a)To expedite the progress of the work of his subcommittee, and to render to the Chairman of the parent Technical Committee such reports on the progress of the work as may be required by the Chairman.

(4a)To make such expenditures for incidental expenses from the annual budget of the subcommittee as he deems necessary.

(5a)To present to the Chairman of the Technical Committee any reports or other matters requiring decision by the Chairman, the Coordinator of Technical Committee Activity, Council, or the Association.

(6) Technical Committee Board

(a) There shall be a Technical Committee Board which shall be composed of the Coordinator of Technical Committee Activity and the Chairman of all Technical Committees. The Coordinator shall be the Chairman of the Technical Committee Board.

(b) The Technical Committee Board shall meet at least once each year for the purpose of reviewing the scope of Technical Committee Activities, making recommendations relative to Committee jurisdiction on individual problems, on assignment of problems, and on such other matters as it deems necessary to expedite the progress of Technical Committee work.

(c) The duties of the Technical Committee Board shall be only advisory to the Coordinator of Technical Committee Activity."

Amendment 19. Article VIII, Section 4, shall be amended by adding the following sentence:

"In calculating the cost of reprints, it shall be proper for the Editor to consider not only the price paid by the Journal for reprints, but also indirect costs properly chargeable to the function of furnishing reprints to authors, such as postage and office expenses."

Studies in Chrome Tanning

XVII. Neutralization of Chrome Leather Prior to Coloring and Fat-liquoring*

by EDWIN R. THEIS, Y. NAYUDAMMA, and C. C. KRITZINGER

(From the Division of Leather Technology, Institute of Research, Lehigh University, Bethlehem, Pa.)

After chrome tanning, leather must be washed and neutralized prior to such operations as coloring, fat-liquoring and drying. The neutralizing process consists of the removal by washing of any uncombined chromium salts or neutral salts remaining in the leather, followed by neutralization with some mild alkali of any free acid left in the washed leather and, finally washing the neutralized leather free of the salts formed during the neutralization.

In 1929, Schindler, Klanfer, and Flaschner [1] studied the neutralization of chrome tanned calf skin and thus determined the amounts of total acid neutralized by various alkalies. These workers also investigated the comparative neutralization of the acid present in the grain and, in the middle layers treated with various reagents, after a two hour treatment. In 1934, Riess and Papayannis [2] studied the neutralization of several different chrome tanned hide powders. In 1935, Innes [3], investigated the neutralization of freshly tanned and washed chrome leather and found that the treated leather showed a varying degree of removal of fixed sulfate as a function of the kind and type of reagent used.

In a most interesting series of papers, starting in 1934, Otto [4] investigated the mechanism of neutralization more specifically in relation to its influence upon subsequent processes. He stressed the probable importance of the penetration of neutralizing anions into the fixed chrome complexes.

Theis in 1937 [5] investigated the neutralizing effects of various neutralizing reagents with regard to the change in sulfato acidity.

*Delivered in part before the Wisconsin Tanners Production Club, Milwaukee, Wisconsin, February 1950 and in part before the Annual Meeting of the American Leather Chemists Association, French Lick, Indiana, May 1950.

Despite extensive experimental studies and specific practical knowledge, we still lack the knowledge for a clear understanding of the actual effects of the neutralizing alkali upon the leather. It is the purpose of this paper to give certain experimental data relative to changes obtaining, during neutralization, upon the protein and chrome bound acids.

Swelling Obtaining During Neutralization

The swelling of native and processed collagen and of various other proteins has attracted much attention in the past, and it is surprising to note that no investigation (to our knowledge) has ever been made of the swelling of chrome tanned leathers in acids and alkalies. In order to make such a study, the following experiments were carried out.

A 55 pound classification hide was split into right and left halves and processed in a regular production load, tannage being done in a paddle with a sugar-reduced chrome liquor. The left half of the hide was removed for swelling studies, while the other half was split and given a chrome retannage in the paddle before being used in the swelling experiments.

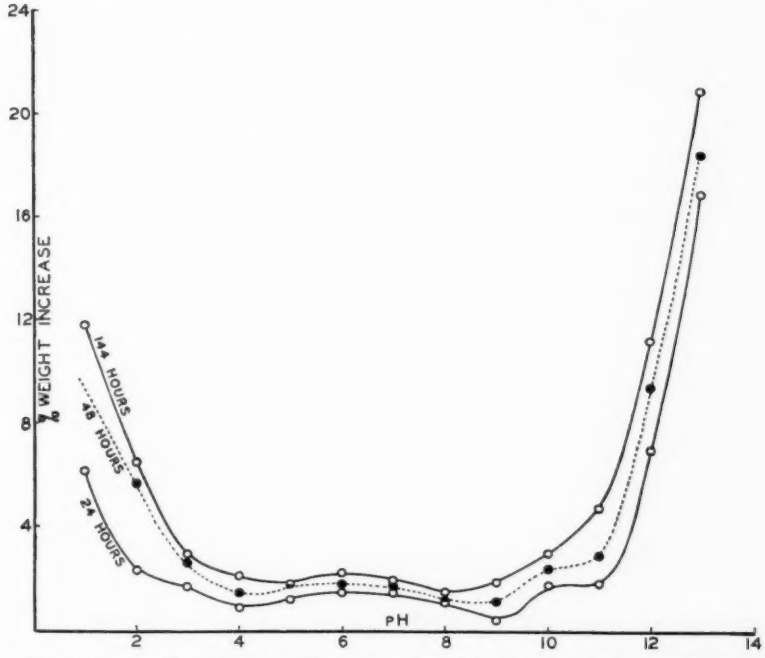


FIGURE 1—Swelling of Chrome Tanned Leather (full thickness) during neutralization in the pH Range 1.0 through 13.0.

Discs of about one inch diameter were cut from the bend portions of the sides and separately milled in water. Milling proceeded for 48 hours in the case of the unsplit side and for 36 hours only in the case of the split retanned side. After this equilibration of the moisture content the discs were blotted for exactly 30 second between sheets of absorbent paper, using a uniform weight to obtain light pressure. This procedure was kept standard throughout the experiments.

Lots of approximately 30 grams were weighed to an accuracy of 0.01 grams on an analytical balance and immersed in 600 ml. of solution, the pH being adjusted to the values listed, in the range 1 to 13, using sulfuric acid and sodium hydroxide.

During the first three days the pH was adjusted as often as feasible, and kept constant within experimental limits. The discs were blotted and weighed after 24, 48 and 144 hours and the increase in weight calculated as percentage swelling increase as shown in Figures 1 and 2.

From this preliminary study, it would appear that swelling of chrome leather takes place to any appreciable extent only in the pH range below 3.0 and above 10. Swelling was somewhat more pronounced in the unsplit side than in the retanned side, indicating that the chrome content of the leather is a factor determining the degree of swelling. It was noticed that chromium

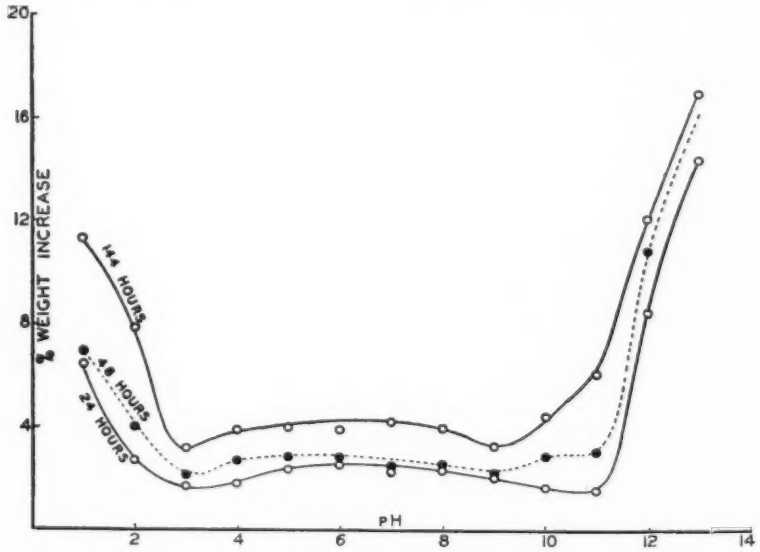


FIGURE 2—Swelling of Chrome Tanned Leather (split to 5.5 ounces) during neutralization in the pH range 1.0 through 13.0.

compounds bled out of the discs kept at low and high pH values, and this bleeding out, i.e. reversal of tannage, might be the prime factor in determining the degree of swelling that will take place, since lightly tanned leathers will be de-chromed at a relatively faster rate. Subsequent studies on the effect of immersion of chrome leather in acid and alkaline solutions upon the chrome content of the leather, to be reported later, adequately demonstrated the rate of de-chroming. Such loss of tannage will release the reactive groups of the protein, which are then free to be hydrated, thereby causing swelling.

It is interesting to note that in the range pH 4 to 8, there is a definite tendency for greater hydration of the protein than at pH 3 to 4 and 8 to 10. Later studies showed that the shrinkage of chrome leather over this pH range is always somewhat lower and it is interesting to speculate as to the cause for this increased hydration. Since the isoelectric point of processed collagen is in the neighborhood of pH 5.0 and the isoionic point at pH 7.0, we would expect a greater number of free charged groups of the protein to exist in this range. Such groups would not only be free to coordinate with water molecules, but their free nature would also be the cause for the shrinkage temperature observed.

The greater degree of swelling in the low and high pH ranges has been attributed to the de-chroming or de-tanning effect of the concentrated acid and alkali, reactive groups such as the amino and carboxyl group thereby being liberated. It would be difficult to prove from these results that the amino group does not enter the chrome complex during tannage, but the writers feel convinced that such actually is the case, and that the swelling of the leather in the low pH ranges is due to the hydration of such free amino groups. These conclusions are based partly on work subsequently done on the shrinkage temperature of the leather and more specifically on the acid binding capacity of the protein in chrome leather.

It will be observed that somewhat greater swelling occurred in the pH range 4.0 to 8.0 in the chrome retanned side, but this is undoubtedly due to the shorter period of milling the discs in water, resulting in unequal moisture content of the discs prior to their being immersed in the acid and alkaline solutions.

Further studies will have to be made of this interesting field. Since the degree of swelling is so much lower than that of native collagen or gelatin, a dilatometer or some such similar system will have to be devised to obtain more accurate results.

The Effects of Neutralization at Given pH Values Upon The Shrinkage Temperature and Cr_2O_3 Content of Chrome Leathers

Previously reported studies from this laboratory and others have indicated that the shrinkage temperature of chrome leather plotted against the equilibrium pH of the immersing solution has a very distinctive curve, and further-

more, that the chrome content of the leather during such immersion varies as a function of the acidity or alkalinity of the solution. The question now arises whether these curves for shrinkage temperature and Cr_2O_3 content would vary with the length of time of soaking the leather at a given pH value, and whether such new information might not throw more light on the nature of the combination between collagen and basic chromium sulfate tanning complexes.

Dried pickled goatskin strips were soaked overnight in an eight per cent sodium chloride solution, the liquor replaced by a fresh solution of 4 per cent sodium chloride for six hours, again discarded and replaced by fresh 4 per cent sodium chloride to which the one-third basic sulfur dioxide-reduced chrome liquor was then added. Tannage proceeded for seven days at room temperature (about 25°C.), the pH of the tanning bath being adjusted at intervals to approximately 3.3. No adjustment of the pH occurred during the last two days of tanning, and the equilibrium pH of the tanning bath was 2.85. The strips showed a chromium content of 6.55 per cent Cr_2O_3 on a protein basis after pressing three times at 10,000 pounds per square inch. The tanned strips were washed in running water for fifteen minutes to remove excess chrome liquor prior to immersion in the neutralizing solutions. These strips were to be used for determination of the shrinkage temperature.

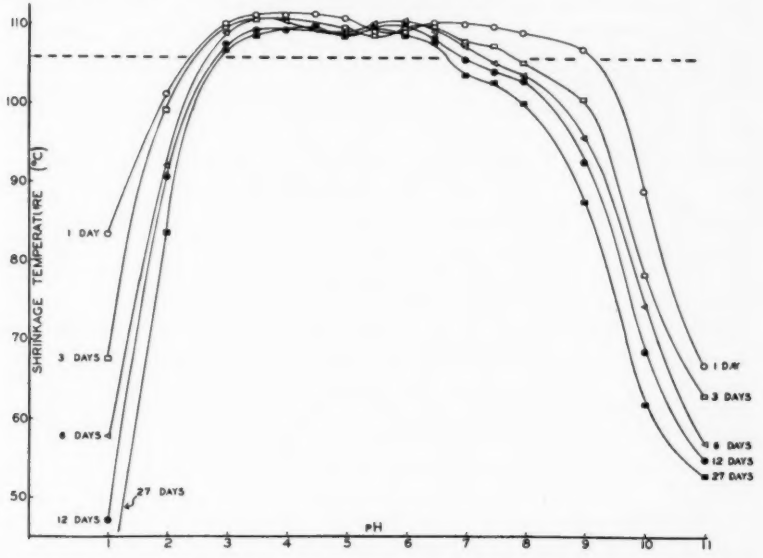
In order to study the change in chrome content of the leather, a batch of standard hide powder was tanned under conditions similar to those discussed above for the strips, omitting the initial soak in 8 and 4 per cent sodium chloride solutions, and again tanning the powder in a chrome liquor containing 4 per cent sodium chloride on the solution. After tanning was completed, the powder was pressed three times at 10,000 psi, dried, ground in a Wiley mill and then soaked back in distilled water in a shaker for twenty hours. The wet chromed powder was filtered off and divided into approximately equal lots for immersion with a number of strips in the appropriate solutions. The pressed powder showed a chrome content of 6.86 per cent Cr_2O_3 on a protein basis.

The solutions were adjusted to the following pH values, using sulfuric acid and sodium carbonate to obtain and maintain each given pH value: 1.0, 2.0, 3.0, 3.5, 4.0, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 9.0, 10.0, and 11.0. Frequent adjustment of the pH was required during the first three days of soaking.

The shrinkage temperature* of the strips was determined after 1, 3, 6, 12, and 27 days, using three strips for each determination. At the same time a sample of the chromed powder was removed from the bath, pressed, dried, re-ground and analyzed for Cr_2O_3 content. It should be pointed out here that the chromed powder in the solution kept at pH 1.0 was rapidly digested by the acid and that all the powder had gone into solution after eighteen days,

*Shrinkage temperatures were determined through the use of the Pressure Shrinkage Meter—described in *this journal* **44**, 548 (1949).

hence the chromium content of pressed strips had to be determined in this case after 27 days of soaking. No determination of the chromium content of the powder was done for the third day of soaking.



FIRURE 3—Shrinkage temperature of Chrome Tanned Leather after neutralization.

The results obtained are shown in Figures 3 and 4. It will be noted that a datum line (D) is shown in the shrinkage temperature curves. This line represents the initial shrinkage temperature (106°C.) of the strips immediately after completion of tannage, and is included to indicate the changes taking place above and below the equilibrium pH value of the stock. The data given in Figure 3 are of real practical importance when we consider the neutralization of chrome tanned leathers. These data indicate that the shrinkage temperature of the neutralized leather increases in the pH range 3.0 to 10.0 (24 hour neutralization). For the 24 hour neutralization period, a minimum shrinkage point is indicated at approximately pH 6.0. As the period of neutralization is increased, the shrinkage temperature over the entire pH range decreases but in the range 3.0 to 6.75 (27 days) the shrinkage temperature is still above that of the original unneutralized leather. At pH values less than 3.0 and greater than 7.0, the shrinkage temperature of the leather decreases sharply with subsequent bleeding out of the originally fixed chromium salts, especially in the acid range. As the neutralizing period is increased, the minimum point in the shrinkage temperature curves shifts from approximately

pH 7.0 to pH 5.0. The indication of the two maxima and a minimum point in the shrinkage temperature curves in the pH range 3.0 to 9.0 has been indicated previously by Theis and Kleppinger[6]. The further substantiation of these particular trends in the shrinkage temperature curves and in this particular pH zone, in the present work, leave but little doubt that they exist.

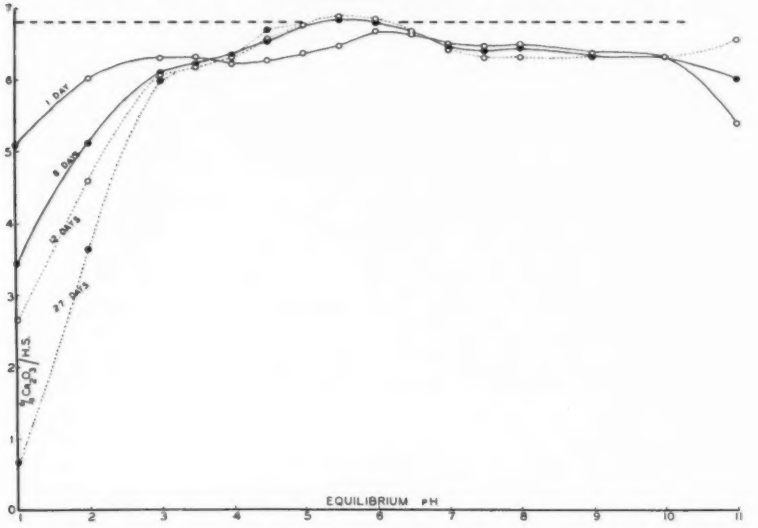


FIGURE 4—Cr_2O_3 content of Chrome Tanned Leather after neutralization in the pH range 1 to 11.

Neutralization of chrome tanned leathers at pH values greater than 6.0 has presupposed the formation and precipitation of hydrous chromic oxides within the leather. The data given in Figures 3 and 4, relative to shrinkage temperature and Cr_2O_3 content of the leather neutralized at still higher pH values, leads to other interesting speculation. At pH values less than 5.0, chromium fixation has been thought of as more or less cationic binding. Long neutralization at higher pH values, however, appears to change the chromium complex from the cationic type to one of non-ionic or even anionic character without formation or precipitation of hydroxide within the leather. Certain of the data, relative to shrinkage temperature of leather neutralized at these higher pH values, would indicate such postulation to be true.

The Effects of Different Alkalies Used as Neutralizing Agents

In order that results obtained through the use of different alkalies could be correlated, all experiments were conducted on stock tanned in one batch as follows.

Goatskin strips (previously pickled and dried) which were to be used for shrinkage temperature determinations were soaked back overnight in 3 liters of 8 per cent sodium chloride solution, the solution replaced by 4 per cent sodium chloride and the necessary amount of one-third basic sulfur dioxide-reduced chrome liquor added. Tannage proceeded for seven days at room temperature, the pH of the tanning bath being adjusted with sodium bicarbonate at intervals to approximately 3.4. The final equilibrium pH of the solution was 3.0 and the strips showed a shrinkage temperature of 106°C., the datum line (D). The Cr_2O_3 content of pressed dried strips was 7.40 per cent based on hide substance. The tanned strips were pressed three times at 10,000 psi and bottled for subsequent use.

For studies on the protein bound acid, sulfato-acidity of the chromium complex, etc., chrome tanned hide powder was prepared by the same procedure as for the goatskin strips, except that the initial soak in 8 per cent sodium chloride was omitted. After completion of tanning, the powder was pressed, dried at room temperature, ground in a Wiley mill and bottled. This tanned powder showed 7.72 per cent Cr_2O_3 based on hide substance.

Three strips and a sufficient quantity of powder to bring the final weight to exactly seven grams were used in each case. The stock was put into beakers with 600 ml. of water for a few hours, a few drops of octyl alcohol being added to assist in wetting back, and the pH then adjusted by means of the appropriate alkali, taking care to measure the exact amount of standard alkal required to obtain and maintain a given pH. The pH range covered the following points: 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 10.0, 11.0, and 12.0. For the pH range below 3.0 sulfuric acid was used, and as alkalies sodium hydroxide, trisodium phosphate, sodium carbonate, borax, sodium bicarbonate and ammonium bicarbonate. Frequent adjustment of the pH was necessary, and the stock was kept immersed for six days since equilibrium could not be attained in a shorter time. In order to calculate the amount of alkali required per gram of dry leather to equilibrate the stock at a given pH, corrections were made for the alkali required to obtain the same pH in the same volume of water, and the alkali then calculated as millimoles per gram of leather (on a moisture-free basis) as well as on a percentage basis on the leather. It should be pointed out that it was difficult in all cases to measure accurately the alkali required in the extreme ranges for each individual alkali, hence the recorded values are only approximate.

After six days, the shrinkage temperature of the three strips in each beaker was determined under constant conditions of heating. The values thus obtained are given in Figure 5.

The powder was filtered off, pressed as before, dried and ground in a small Wiley mill. Exactly 2.0 grams of powder were weighed into separate conical flasks for extraction of the protein bound acid by the method of Merrill et al [17]. At the same time, the protein content of the powder was determined in each

sample. In using the extraction method of Merrill and co-workers, we used 0.04 N NaOH with methyl red as indicator and measured accurately from a micro-burette the total amount of alkali required to neutralize the acid bleeding out of the leather. This alkali was then calculated as milliequivalents H ion per gram of protein as shown in Figures 6, 7, and 8. After this neutralization process, the powder was filtered off and washed, and the sulfate in the filtrate and washings determined as Barium Sulfate. The values obtained have been calculated as milliequivalents sulfate per gram of protein.

The powder was now digested with nitric and perchloric acids and the chromium determined by electrometric titration with standard ferrous chloride, in such a manner that no sulfate was introduced into the solution. After determination of the chromium, a small excess of ferrous chloride was added and the solution filtered before precipitating the sulfate as barium sulfate. The results thus obtained were calculated as *sulfatoacidity of the chrome complex* as shown in Figures 9 and 10. The expression "basicity" becomes meaningless, since we are only determining the sulfato groups bound to the chromium atom.

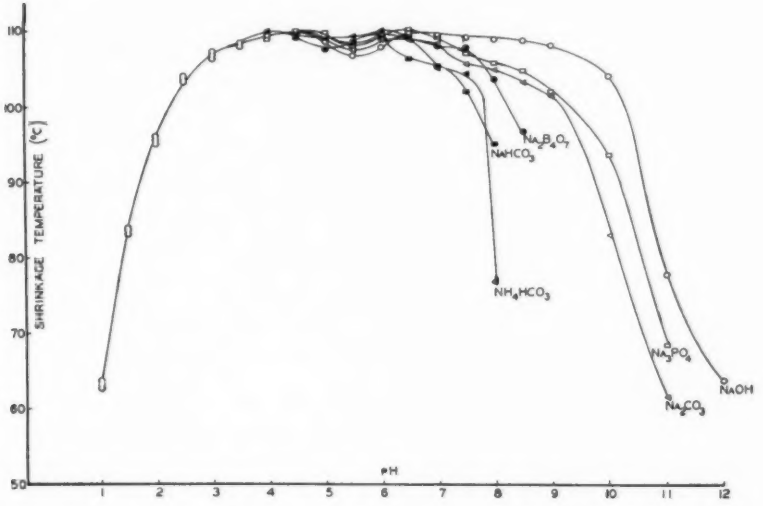


FIGURE 5—Change in shrinkage temperature during neutralization with different alkalies.

Figure 5 shows the shrinkage temperature values of the neutralized leather for each of the alkalies used. These data are of real importance and lead to interesting postulations. Using sodium hydroxide as the neutralizing agent, we find the shrinkage temperature of the treated leather is higher than the

untreated in the pH range 3.0 to 9.5. Below pH 3.0 and above pH 9.5 the shrinkage temperature sharply decreases. Again there appears two maxima (pH 4.0 and 7.0) and a minimum value at pH 5.5 if sodium bicarbonate, ammonium bicarbonate, or borax is used as the alkaline neutralizing agent, a distinctly different trend is noted; namely, a sharp decrease in shrinkage temperature at pH values greater than 7.0. Comparing the trends obtaining for the bicarbonates and borax with that for sodium hydroxide, it can be suggested that the bicarbonates and borax coordinate with the chromium atom to a much greater extent and that these coordination compounds are to a great extent non-tanning in nature at pH values greater than 7.0. Apparently the complexes, formed by the slow addition of the strong alkali,

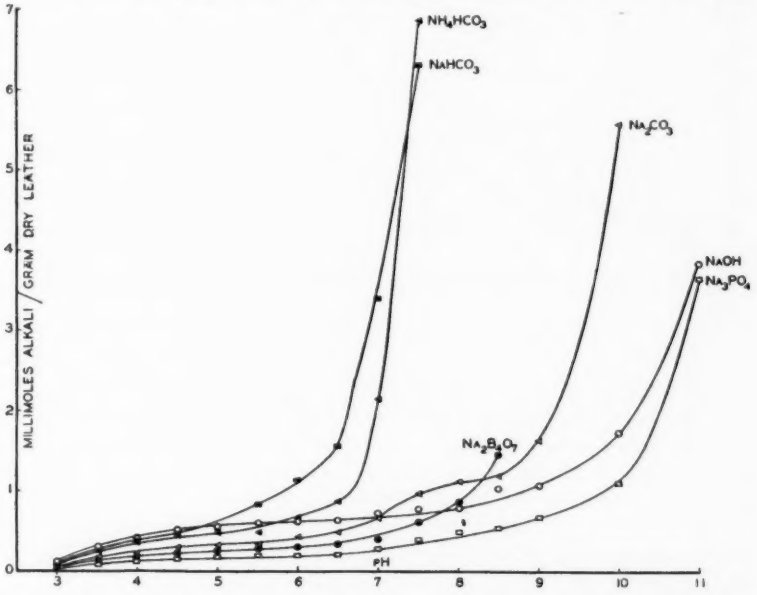


FIGURE 6—Millimoles of specific alkali added, in neutralization, per gram of dry leather.

sodium hydroxide, have greater tanning properties as can be noted by the trend of the shrinkage temperature curve. It is quite possible that the addition of sodium hydroxide causes a gradual change from the cationic to the anionic complex. Sodium phosphate and sodium carbonate are complex formers but here again the complexes formed have greater tanning properties than the bicarbonates or borax.

Figures 6 and 7 show percentage-wise, on a dry leather basis, the amount of the various neutralizing alkalies necessary to bring the neutralized leather

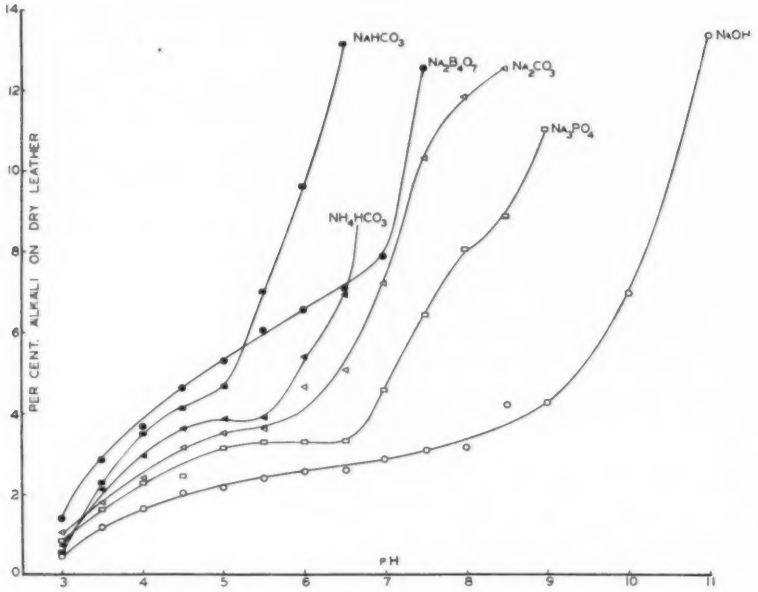


FIGURE 7—Amount of specific neutralizing agent needed for neutralization in the pH range 3 to 11.

to pH values greater than 3.0. These data are significant and indicate why the shrinkage temperature measurements were so different for the bicarbonates versus sodium hydroxide. Thus it can readily be seen that if we should desire to neutralize this particular chrome tanned leather to pH 6.0, it would require 2.5 per cent sodium hydroxide, 4.5 per cent sodium carbonate, 5.5 per cent ammonium bicarbonate, 6.5 per cent borax and 9.6 per cent of sodium bicarbonate. These percentages of alkali would indicate that there is real penetration of the anions into the chromium complex.

Figures 8 and 9 show the amount of protein bound acid of the neutralized leather, in the pH range 1.0 to 7.0 for the various alkalies used as neutralizing agents. The protein bound acid was determined by the best method known at this time, and while a certain error exists, no better method is presently available. These data would appear to indicate that the amount of acid bound with the protein is essentially that bound by untanned collagen and further indicate that the free amino groups of collagen play little role in the chrome tanning reaction. Independently, the Leather Industries Research Institute of South Africa[8] and Weir and Carter[9] of the National Bureau of Standards have arrived at this latter conclusion. If this postulation can be

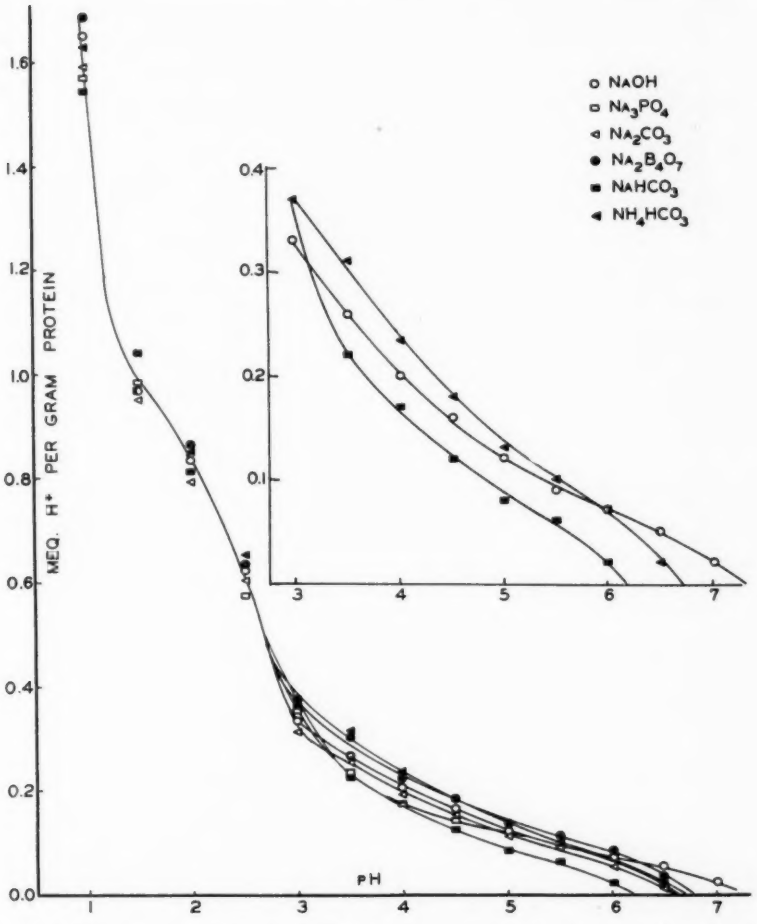


FIGURE 8—Protein bound acid obtaining after neutralization by some six different alkalies.

proved by other workers in this field, it will be a very valuable contribution to the theories of chrome tanning. Present theories suggest that the free amino groups were bound in the chromium complex through coordinate valence. These present data would seem to refute such postulations.

Figure 10 shows the sulfato acidity of the particular chromium complex fixed on the skin proteins in the pH range 2.0 to 10.0 for the several neutraliz-

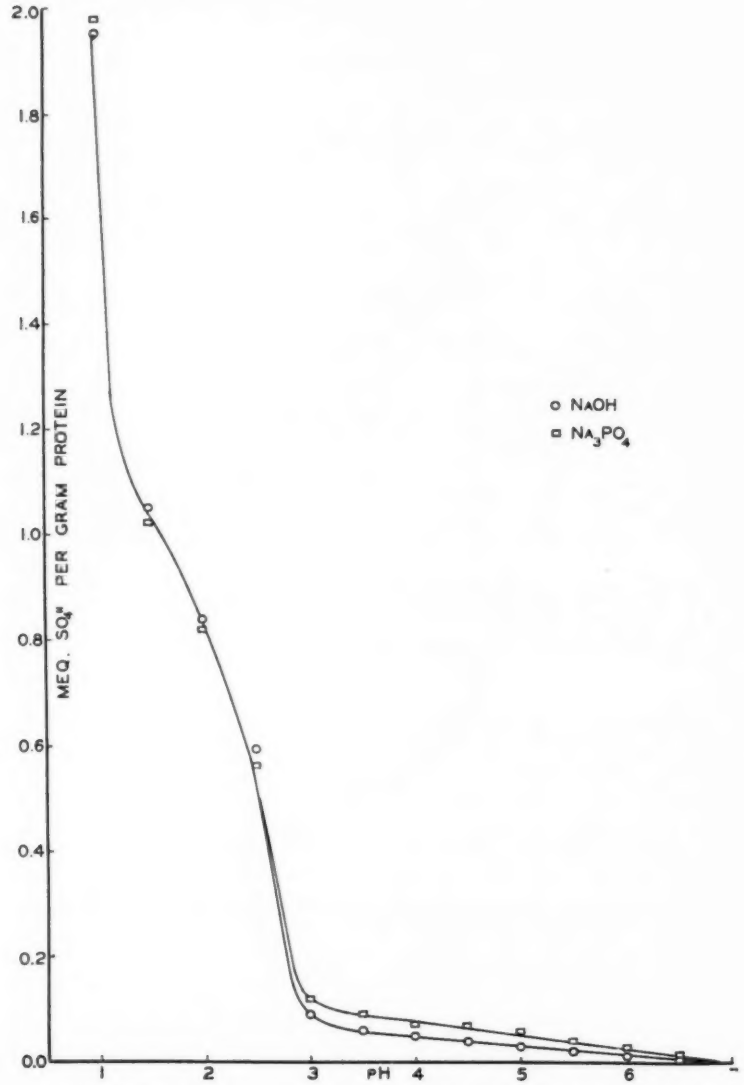


FIGURE 9—H_2SO_4 bound by Chrome Tanned Leather in the pH range 1 to 7.

ing agents. It must be definitely borne in mind that these data represent the *sulfato acidity* and not the *total acidity* of the complex. Since we know that

such anions as phosphate, borate, carbonate, etc., penetrate the complex in varying degrees, they will then, because of this penetration, affect the acidity of the chromium complex in the proportion and degree of their individual penetration. These data, again, show the wide difference between the action of sodium hydroxide and the other neutralizing agents used.

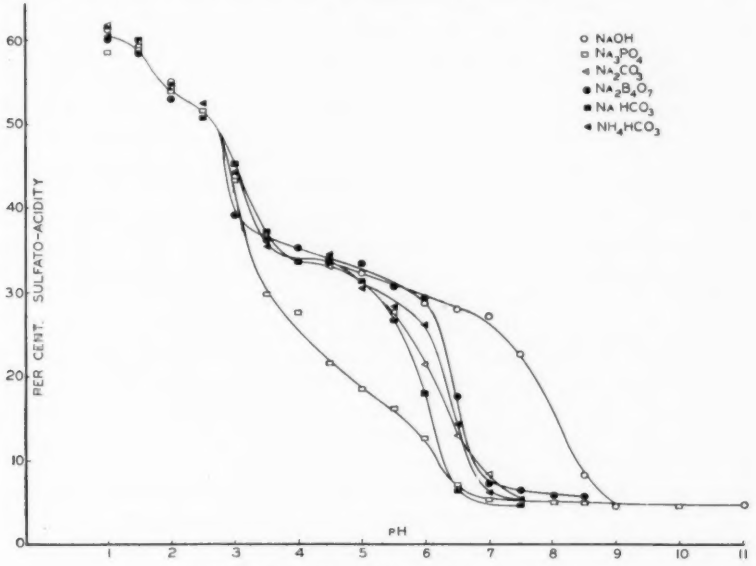


FIGURE 10—Sulfato Acidity after neutralization.

Layer-wise Studies of Neutralization

The previous studies have all dealt with either the neutralization of chrome tanned hide powder or chrome tanned goat skin strips. In 1948 Kritzinger and Theis [10] developed, into a working tool, methods for splitting skin into 10 or more layers so as to study the distribution of tanning materials, fats, dyes, etc., layer-wise in the skin. Since that time, the various analytical methods have been modified and improved so as to be used in the small tannery analytical laboratories.

Three quarter inch diameter buttons were taken from 100 sides of freshly neutralized fully chrome tanned leather. These buttons were split into 10 layers by means of a freezing microtome. After sectioning the layers were air-dryed and ground in a small Wiley mill.

The following methods are an adaptation of those used in the previous studies. The pH of each layer in quadruplicate at least is directly taken by

pressing the section against the electrodes (glass electrode), taking the grain as the first layer. Care must be taken not to wet the discs or sections.

The ground samples are kept stoppered to avoid changes in moisture content. On each sample, the protein content is determined by conventional methods.

Exactly two grams of ground powder are weighed into 250 ml. conical flasks, covered with 50 ml. water and shaken up thoroughly for 15 minutes under high vacuum. A few drops of iso-octyl alcohol will assist in re-wetting. The powder sticking on the sides of the flask is washed down with 50 ml. of water, ten drops of methyl red indicator added and the solution titrated once with 0.05 N NaOH, using a micro-burette. This titration is repeated after three hours and the samples left overnight. During the day the samples are occasionally shaken by hand and titrated every half hour for the first three hours, then every hour for the next five hours. Leave overnight again, and titrate only once to a clear end-point (pH about 5.5). The total volume of alkali added from the burette during this entire period is recorded and calculated in terms of milligram equivalents of acid (H^+) per gram of protein.

$$\text{Mg. equiv. acid } (H^+) = \frac{a \times b}{2} \times \frac{100}{C}$$

where a=ml. alkali added from burette
b=normality of alkali
c=protein content of sample

and using 2 grams powder.

After the last titration, the solution is filtered through No. 40 paper and well washed. The filtrate and washings are combined, made slightly acid to methyl red and the sulfate determined by precipitation with barium chloride. This sulfate is calculated as milligram equivalents protein bound sulfate per gram of protein.

$$\text{Mq. equiv. } SO_4^{=} = \frac{a}{b} \times \frac{1}{2} \times \frac{100}{C} \times 1000$$

where a=wt. of $BaSO_4$ precipitated
b=equivalent wt. of $BaSO_4$
c=protein content

and using 2 grams of powder.

The powder and the filter paper are transferred back to the conical flask, 15 ml. concentrated HNO_3 and a few *clean* glass beads added and the mixture digested on a hot-plate for 10 minutes to break up the paper. Care must be taken to avoid excessive bumping. Add 20 ml. concentrated perchloric acid and digest until the chromium is oxidized to the hexavalent state. Cool for a minute, add 100 ml. water, boil for 10 minutes, cool and titrate the chromium with *ferrous chloride* (about 0.2 N strength). At the end of the titration add a small excess (about one milliliter) ferrous chloride. For this titration the solution has to be transferred to a beaker and back to the conical flask (or

other vessel) again, and care must be taken to avoid any loss. The solution is filtered and washed to remove any insoluble matter commonly present in leathers. Determine the sulfate in the combined filtrate and washings. Calculate (1) the milligram equivalents chromium and (2) the milligram equivalents sulfate present in the *total* sample taken, then calculate (3) the sulfato-acidity of the chromium complex, (4) the milligram equivalents Cr_2O_3 per gram of protein and if necessary (5) the per cent Cr_2O_3 on a protein basis.

(1) Mg. equiv. Cr = ml. $FeCl_2$ x normality of $FeCl_2$

(2) Mg. equiv. $SO_4 = \dfrac{\text{wt. } BaSO_4}{\text{equiv. wt. } BaSO_4} \times 1000$

(3) Sulfato acidity $= \dfrac{\text{mg. equiv. } SO_4}{\text{mg. equiv. Cr}} \times 100$

(4) Mg. equiv. Cr. per gram protein $= \dfrac{(1)}{2} \times \dfrac{100}{\text{protein content}}$

(5) Per cent Cr_2O_3 per Hide Substance $= (4) \times \dfrac{152}{6000} \times 100$

Exactly one gram of leather is boiled with 40 ml. of three per cent NaOH for 30–60 minutes, preferably under reflux. Cool and neutralize with HNO_3 until just acid to phenolphthalein, filter and wash well, combining the filtrate and washings. Add 10 ml. concentrated HNO_3 and 5 ml. 5 per cent $AgNO_3$ and digest for one to two hours at the boil. Filter through a prepared Gooch, wash well with water and three times with chloroform to remove any fatty acid material left on the asbestos bed. Dry and weigh. Calculate the chloride as milligram equivalents per gram of protein.

$$\text{Mg. equiv. } Cl^- = \frac{\text{Wt. of AgCl}}{\text{equiv. wt. of AgCl}} \times 1000 \times \frac{100}{\text{protein content}}$$

A blank determination should be made on the NaOH.

Exactly one gram of leather is digested with 10 ml. HNO_3 and 10–15 ml. perchloric acid to near dryness, using a few glass beads to avoid undue bumping. Dissolve in 25–30 ml. distilled water, filter, wash well and make up the filtrate plus washings to a convenient volume (say 100 ml.) Determine sodium on the flame photometer and express as milligram equivalents per gram of protein.

In the table the sodium has been calculated as per cent NaCl (on a protein basis), the remaining chloride as HCl and the protein bound sulfate as H_2SO_4. Actually the sum of the milligram equivalents of Na^+ and H^+ equals (within experimental limits) the sum of milligram equivalents of $SO_4^=$ and Cl^-.

Basicity is expressed in the conventional manner, viz. 100 per cent—sulfato acidity.

Table 1 and Figures 11 and 12 give the data obtained for this particular commercially tanned and neutralized side leather. It must be borne in mind that these data are real average values from 100 sides and, therefore, may be

TABLE I

Stratigraphic Analysis of Paddle-tanned Leather after Neutralization

Layers	pH	Sulfato Acidity	Mg. equiv. per gm. Protein Cr_2O_3 Bound	Protein Bound H	Protein Bound SO_4	Na	Cl	Basicity*	Per Cent** Cr_2O_3	HCl	H_2SO_4	NaCl
1	4.54	28.7	2.10	.47	.25	2.81	2.98	71.3	5.33	.62	1.22	16.41
2	4.47	26.4	2.06	.50	.18	2.19	2.46	73.6	5.21	.98	.88	12.81
3	4.44	24.0	2.16	.50	.08	1.37	1.84	76.0	5.47	1.71	.39	8.02
4	4.40	22.2	2.28	.50	.06	1.15	1.68	77.8	5.77	1.93	.29	6.73
5	4.41	23.2	2.20	.49	.05	1.06	1.61	76.8	5.57	2.00	.24	6.20
6	4.42	23.0	2.13	.48	.05	1.06	1.49	77.0	5.40	1.57	.24	6.20
7	4.42	23.3	2.04	.48	.06	1.15	1.63	76.7	5.18	1.75	.29	6.73
8	4.37	23.7	2.17	.49	.06	——	1.73	76.3	5.51	——	.29	——
9	4.36	24.0	2.08	.48	.09	1.36	1.75	76.0	5.29	1.42	.44	7.96
10	4.32	26.1	1.89	.50	.10	1.33	1.84	73.9	4.79	1.86	.49	7.79

*100 Per Cent—sulfato acidity.
**Hide substance basis.

considered to represent the true picture of the leather made in this particular tannery.

Figure 11 shows data plotted in such a manner as to show percentagewise while Figure 12 pictures the data along purely chemical lines. This last Figure will allow simple calculate to other terms and units if desired. Discussion of these Figures will be held in abeyance until later in this paper.

Pilot Plant Scale Neutralization Tests*

Preliminary investigations have indicated (1) side leather after neutralization can easily be split into a satisfactory number of layers by the United Shoe Machinery Corporation Model "A" Splitting Machine, and (2) these layers can then be analyzed for Cr_2O_3, hide substance, fatty matter (free and bound), protein and chromium bound acid and thus, the approximate nature of the sulfato chromium complex determined.

Medium weight stock, for smooth leather, was used for these investigations. One hundred (100) pounds of chrome tanned (regular formate tannage) stock, shaved weight were taken for each of the individual tests. The stock was floated with 200 per cent (25 gallons) water at 100° F., drummed 20 minutes, the stock drained and again floated with 25 gallons water at 100°F.

To the floated stock was then added; *test No.* 1 no neutralizing agent, *test No.* 2 one-half per cent neutralizing agent, *test No.* 3 three-quarters per cent neutralizing agent, *test No.* 4 one per cent neutralizing agent, *test No.* 5 one and one-quarter per cent neutralizing agent, *test No.* 6 one and one-half per cent neutralizing agent, *test No.* 7 two per cent neutralizing agent, and *test No.* 8 two and one-half per cent neutralizing agent.

*The bating, pickling and chrome tannage used for these tests was that normally used for all stock in this plant—drum, bating, pickling and tanning (one operation). The sodium formate used was added during the last 10 minutes of pickling. The chrome liquor used was an approximately 40 per cent basic sugar reduced liquor. The complete operation of bating, pickling and tanning was some 7 hours.

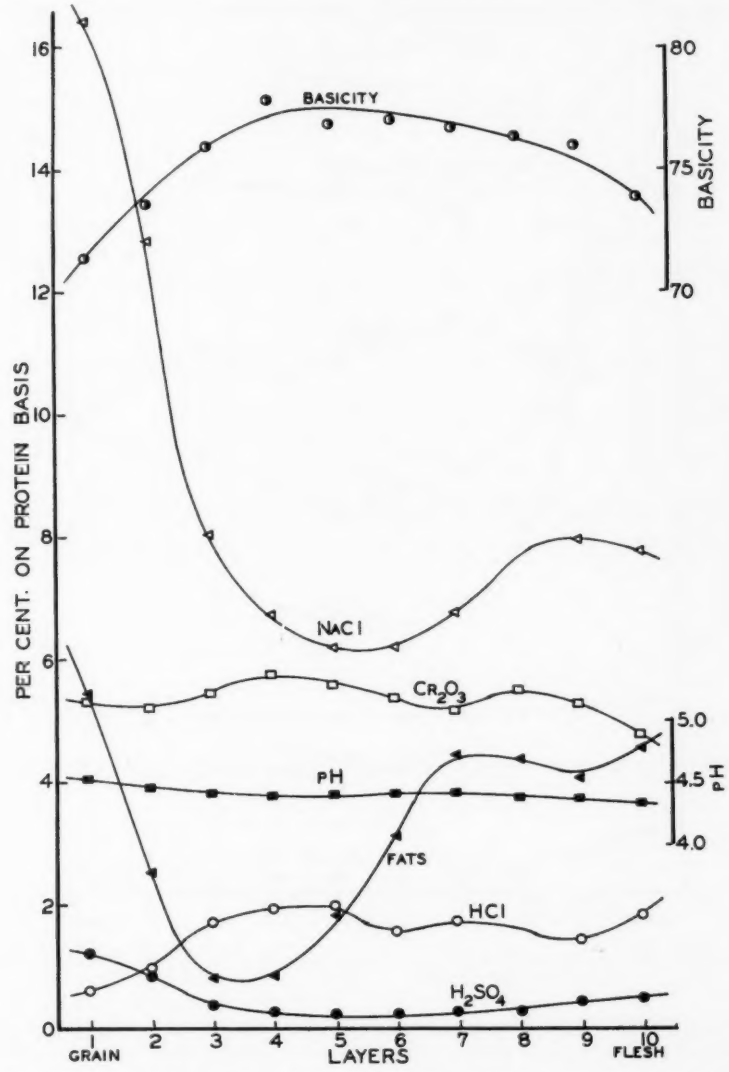


FIGURE 11—Stratigraph of neutralized chrome leather all constituents calculated percentage-wise.

After 30 minutes drumming with the neutralizing agent, the stock was drained and floated with 16 gallons of water at 80°F. and was ready for sub-

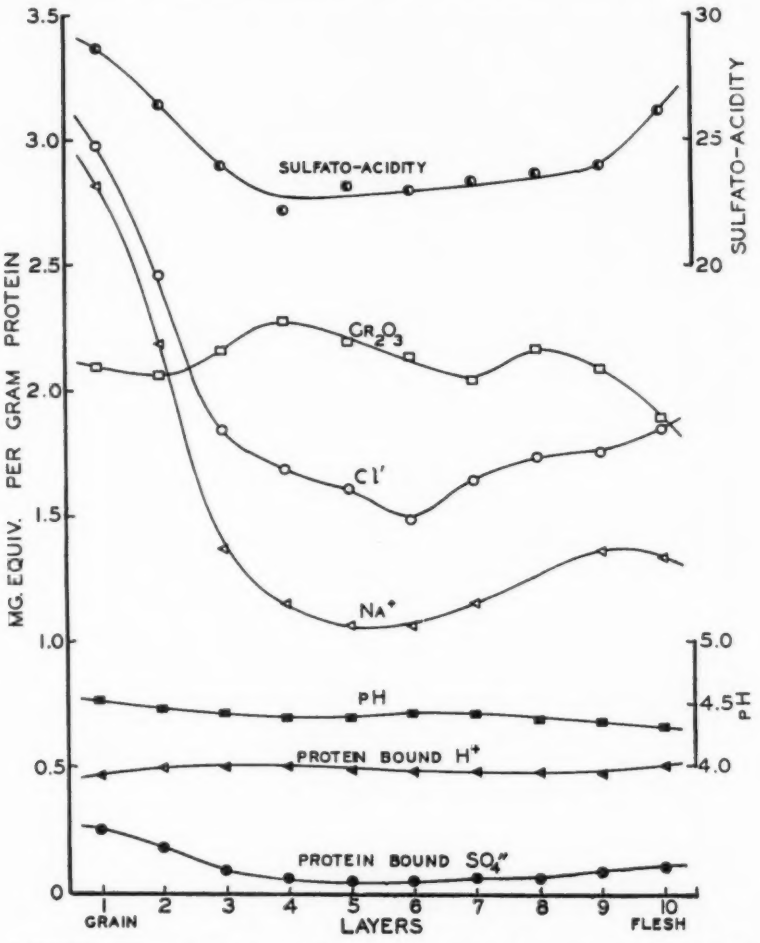


FIGURE 12—Stratigraph of neutralized chrome leather all constituents calcluated in miliequivalents.

sequent operations. Samples of the leather (position 2) in strips 3" x 8" were taken from each side; 1, immediately after neutralization, and 2, in the *crust sort*.

The data taken for the pilot plant tests are given in Table 2 and in Figures 13, 14, and 15. These data are of real interest in that they show specifically the changes taking place during the neutralizing process and for three of the

Experimental Data Taken

Sodium Bicarbonate Series

Neutralization with Sodium Bicarbonate

Drain stock and float with 25 gallons water at 100° F. and then add neutralizing agent.

Test No.	1	2	3	4
Per cent Sodium Bicarbonate added	0.00	0.50	0.75	1.00
pH of Liquor after 30 minutes drumming	4.03	6.17	6.59	6.68
Test No.	5	6	7	8
Per cent Sodium Bicarbonate added	1.25	1.50	2.00	2.50
pH of Liquor after 30 minutes drumming	6.78	6.91	7.06	7.12

Borax Series

Neutralization with Borax

Drain stock and float with 25 gallons water at 100° F. and then add neutralizing agent.

Test No.	1	2	3	4
Per cent Borax added	0.00	0.50	0.75	1.00
pH of Liquor after 30 minutes drumming	4.03	4.57	5.02	6.00
Test No.	5	6	7	8
Per cent Borax added	1.25	1.50	2.00	2.50
pH of Liquor after 30 minutes drumming	6.75	7.00	7.60	7.61

Ammonium Bicarbonate Series

Neutralization with Ammonium Bicarbonate

Drain stock and float with 25 gallons water at 100°F. and then add neutralizing agent.

Test No.	1	2	3	4
Per cent Ammonium Bicarbonate Added	0.00	0.50	0.75	1.00
pH of Liquor after 30 minutes drumming	4.01	6.21	6.60	6.93
Test No.	5	6	7	8
Per cent Ammonium Bicarbonate added	1.25	1.50	2.00	2.50
pH of Liquor after 30 minutes drumming	7.08	7.12	7.30	7.39

TABLE II

Sulfato Acidities

	Per Cent Neutralizer Used							
	0	0.5	0.75	1.0	1.25	1.5	2.0	2.5
Sodium Bicarbonate Series								
Grain	28.1	29.5	28.2	28.2	23.0	28.9	25.4	24.5
Middle	25.1	32.7	31.3	32.0	33.0	30.4	30.5	31.7
Flesh	24.6	24.7	23.8	22.0	22.2	20.1	17.9	18.8
Borax Series								
Grain	25.6	24.3	24.6	24.6	22.0	18.6	16.5	15.1
Middle	22.2	25.2	23.0	24.1	22.3	20.6	20.5	21.1
Flesh	23.6	21.2	22.8	21.7	18.8	17.2	15.0	15.2
Ammonium Bicarbonate Series								
Grain	36.4	38.0	40.5	34.7	33.4	31.8	29.9	32.2
Middle	36.6	36.6	33.3	33.8	37.0	36.7	37.6	25.1
Flesh	37.6	32.0	23.8	22.6	25.1	27.4	26.1	23.2

most important chemicals used in this process. Figures 13 and 14 picture the data for the sodium bicarbonate and the borax neutralization series—the concentration of neutralizing chemicals varying from 0 to 2.5 per cent based on blue shaved weight. These data indicate strikingly that regardless of the amount of chemical used, the protein bound acid remains essentially constant in the center of the skin. In other words, the internal acidity is not changed under the conditions of neutralization obtaining when using these two alkalies. However, when sodium bicarbonate is used, the grain and flesh layers are drastically changed with reference to protein bound acid, as the concentration of the alkali is increased. The same conditions obtain for the borax neutralization with the exception that in no case do we have negative acidity as is the case for sodium bicarbonate.

Figure 15 shows the data taken for the ammonium bicarbonate neutralization series and these data indicate an entirely different trend from that given in Figures 13 and 14. In these series of tests, the data show a progressive decrease in protein bound acid in the center layers of the skin as the neutralizing alkali is increased, thus indicating that ammonium bicarbonate penetrates faster and more thoroughly to the center and thus gives a more thorough neutralizing action than that obtaining for sodium bicarbonate or borax. This trend is very important and will be discussed in some detail later in this paper.

The acidities noted in Figures 13, 14 and 15 are those for protein bound acid and have nothing whatever to do with the chromium bound acidities of the chromium complex fixed on the animal skin fiber. Table 2 shows the sulfato acidities for the three series of neutralizing tests made. These sulfato acidities were calculated from the chromium bound sulfate in relation to the

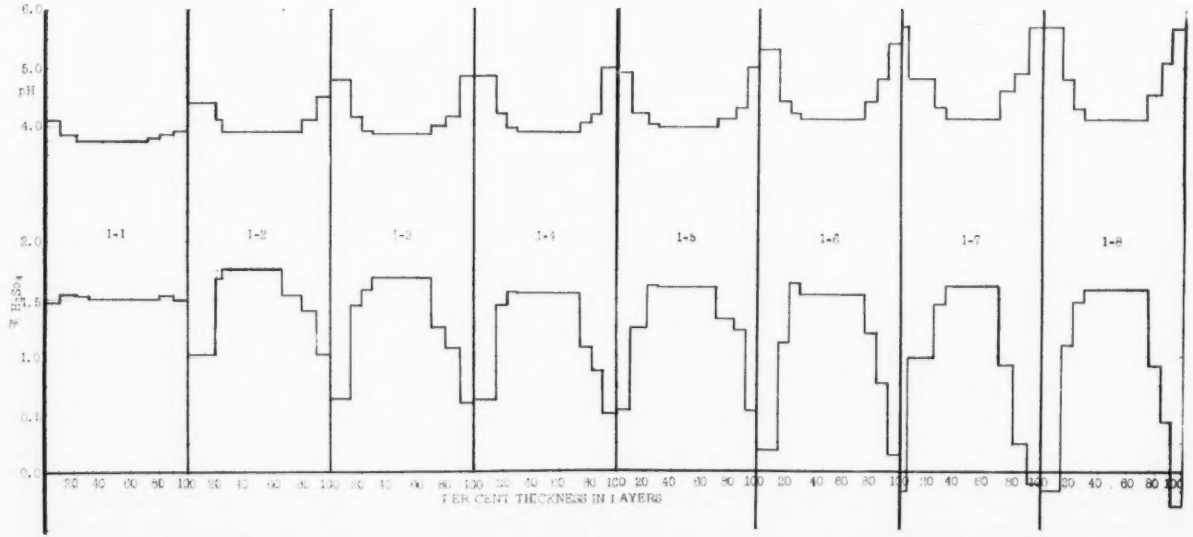


FIGURE 13—Sodium Bicarbonate Series. Showing acid bound to hide substance after varying degrees of neutralization of Chrome Tanned Leathers, (1) 0 Per cent Sodium Bicarbonate added, (2) 0.50 Per cent added, (3) 0.75 Per cent added, (4) 1.00 Per cent added, (5) 1.25 Per cent added, (6) 1.5 Per cent added, (7) 2.00 Per cent added, (8) 2.50 Per cent added. Top Curve represents pH value of Leather and bottom curve that of per cent H_2SO_4 bound by Hide Substance.

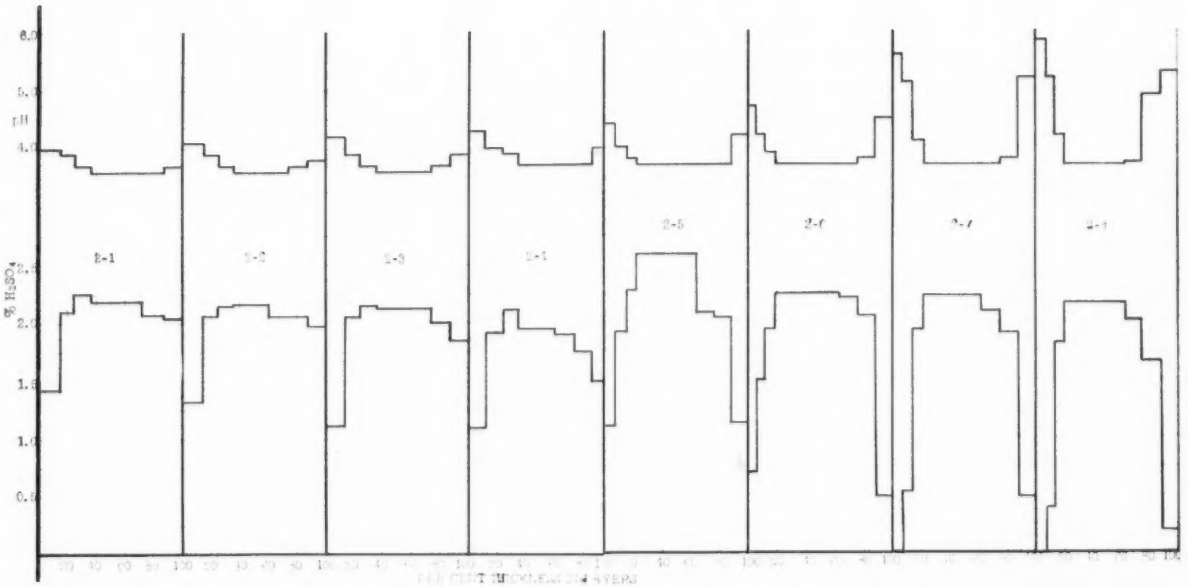


FIGURE 14—Borax Series. Showing Acid Bound to Hide Substance after varying degrees of neutralization of Chrome Tanned Leathers, (1) 0 Per cent Borax added, (2) 0.50 Per cent added, (3) 0.75 Per cent added, (4) 1.00 Per cent added, (5) 1.25 Per cent added, (6) 1.5 Per cent added, (7) 2.00 Per cent added, (8) 2.50 Per cent added. Top Curve Represents pH value of Leather and Bottom Curve that of Per cent H_2SO_4 bound by Hide Substance.

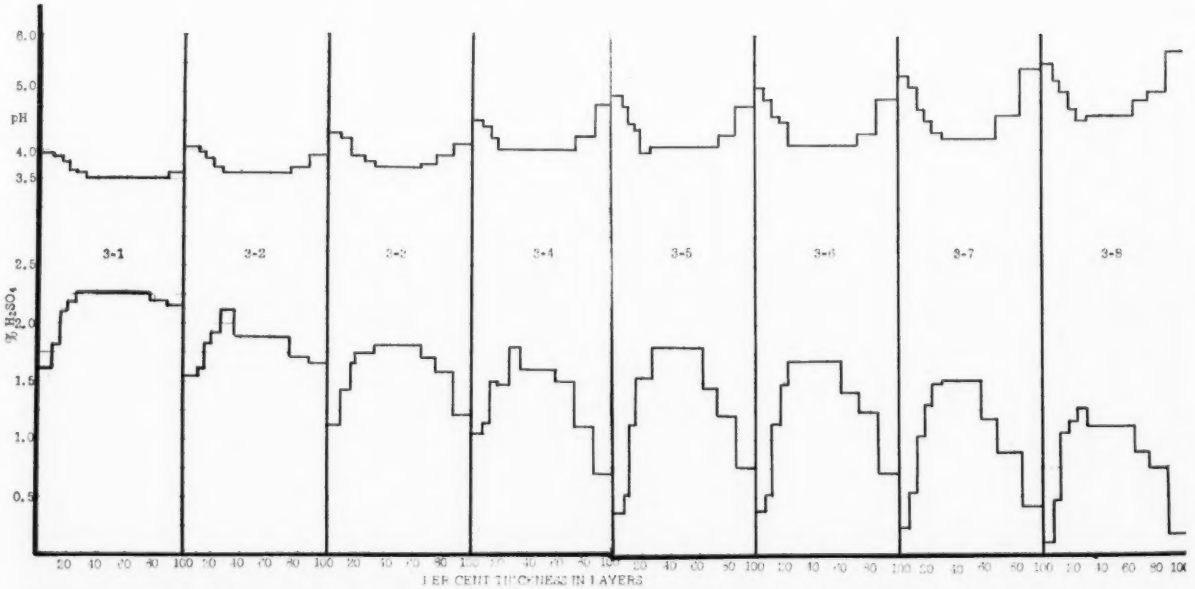


FIGURE 15—Ammonium Bicarbonate Series. Showing Acid Bound to Hide Substance after varying degrees of neutralization of Chrome Tanned Leathers, (1) 0 Per cent Ammonium Bicarbonate added, (2) 0.50 Per cent added, (3) 0.75 Per cent added, (4) 1.00 Per cent added, (5) 1.25 Per cent added, (5) 1.5 Per cent added, (7) 2.00 Per cent added, (8) 2.50 Per cent added. Top Curve Represents pH value of leather and bottom curve that of Per cent H_2SO_4 bound by Hide Substance°

chromic oxide fixed. It is to be noted that for moderate additions of neutralizing agent, the sulfato acidities do not change materially in the center layers of the skin as can be noted by a study of Table 2. The same conclusion is essentially true for the grain layer of the skin whether the neutralizing chemical be sodium bicarbonate, borax or ammonium bicarbonate. This statement, however, is not true for the flesh layers; for the flesh layer, in the case of sodium bicarbonate, the sulfato acidity decreases from 24.6 at 0 per cent alkali to 18.8 using 2.5 per cent sodium bicarbonate. For the borax series and again the flesh layer, the decrease in sulfato acidity in the same range is from 23.6 to 15.2 and for the ammonium bicarbonate series, from 37.6 to 23.2 The decrease in sulfato acidity for the flesh layer is much more pronounced in the case of ammonium bicarbonate as can be seen from the table.

It has already been pointed out in this paper that we do not have an exact method for differentiating the protein bound and the chromium bound acid. McLaughlin and Theis[11] in "The Chemistry of Leather Manufacture" pointed out that probably the most satisfactory analytical method for differentiation of these two types of acid was the method devised by Gustavson[7] and this method was used for the stratigraphic analysis of the several leathers considered in these series of tests. It should be stated in a positive manner that until we are in possession of more satisfactory analytical methods for differentiating the various types of fixed acid in chrome leather, we can determine only approximately the relative values of protein and of chromium bound acid. The writers, however, believe that by using such approximate values as is given by the method of Gustavson, we can point out the trend obtaining for the penetration of various neutralizing agents as are given in this paper.

Conclusion

In this paper, we have discussed various phases of the neutralizing reaction obtaining when chrome tanned leather is treated with alkali prior to coloring and fat-liquoring.

We have shown the effect of neutralization at various pH values on the shrinkage temperature and on the chromic oxide content of chrome leathers. In this regard, it has been postulated that neutralization at pH values greater than 5 appear to change the chromium complex from the cationic type to one of non-ionic or even anionic character, without formation or precipitation of hydroxide within the leather.

We have shown the effects of different alkalies when used as neutralizing agents. Figures picturing these effects are given and these data indicate that sodium hydroxide and sodium carbonate can be used efficiently as far as chromic oxide fixation and shrinkage temperature of the final leather are concerned. We have studied the layer-wise effect of three different neutralizing agents; namely, sodium bicarbonate, borax, and ammonium bicarbonate and

the results of these stratigraphic studies are not only interesting, but of real importance to the leather chemist and practical tanner.

It has long been known that ammonium salts such as ammonium bicarbonate or ammonium hydroxide in conjunction with ammonium chloride tend to give a much more thorough neutralization and usually a softer leather, whereas such neutralizing chemicals as sodium bicarbonate or borax tend to give a somewhat firmer leather. Such postulations have been practical concepts and the literature contains no definite information as to why such results should obtain. The data contained in this paper show rather strikingly as to why leather neutralized with ammonium hydroxide or ammonium bicarbonate tends to give a softer leather. The data readily indicate that ammonium bicarbonate penetrates much more thoroughly and probably faster toward the center of the skin than does sodium bicarbonate or borax. It is believed that a study of the data given in Figures 13, 14, and 15 and in Table 26 will yield results of a practical nature to the tanner.

Acknowledgment

The writers are indebted to the American Cyanamid Company, the Diamond Alkali Company and Mutual Chemical Company of America for funds supporting this investigation and the writers are pleased to acknowledge this generous support and cooperation by this group. The writers would also like to acknowledge the splendid cooperation given by the Albert Trostel and Sons Company of Milwaukee, Wisconsin for the use of their pilot plant for the pilot plant studies given in detail in this paper.

Bibliography

1. Schindler, W., Klanfer, K., and Flaschner, E., *Collegium* **714,** 472, (1929).
2. Riess, C., and Papayannis A., *Ibid.* **769,** 226, (1934).
3. Innes, W. F., *J. Intern. Soc. Leather Trades Chem.* **19,** 190 (1935).
4. Otto, G., *Collegium*, **776,** 597, (1934); **784,** 371, (1935), **822,** 509 (1938).
5. Theis, E. R., *J. Am. Leather Chem. Assoc.*, **32,** 285, (1937).
6. Theis, E. R., and Kleppinger, C. T., *Ibid.* **42,** 591, (1947).
7. Merrill, H. B., Niedercorn, J. G., and Quarck, R., *Ibid.* **23,** 187, (1928); Gustavson, K. H., *Ibid.* **21,** 559, (1926).
8. Monthly Circular, Leather Industries Research Institute, Private Circular.
9. Weir, C. R., and Carter, J., *J. Am. Leather Chem. Assoc.*, **45,** 421, (1950).
10. Kritzinger, C. C., and Theis, E. R., *Ibid.* **43,** 379 (1948).
11. McLaughlin, G. D., and Theis, E. R., The Chemistry of Leather Manufacture, page 442. Reinhold Pub. Co., New York (1945).

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Discussion

I. C. Somerville: I think it is well to note that these experiments are carried out under practical conditions. I should like to ask Dr. Theis if the original chrome tannage was in the presence of a masking agent, like formate?

DR. THEIS: It was.

SOMERVILLE: How long drumming during neutralization?

THEIS: Thirty minutes.

SOMERVILLE: Is the value for acid a total Acidity figure?

THEIS: Total figure by the titration method as given in the ALCA.

SOMERVILLE: I think this is a very good demonstration of the much quicker penetration with ammonium bicarbonate. That is to me the most outstanding part of the whole paper. The results with borax and bicarbonate are more nearly the same and, as Dr. Theis says, a lot of tanners use them interchangeably. Borax is a stronger base than bicarbonate, and the reason why some people think it is a weaker base is because it takes more of it to get the chemically equivalent amount.

Dr. Theis' curves indicate there is no sudden change in acidity in the center as shown by the pH. The actual pH of the center layers went up very smoothly. The interesting jump was in the acidity values. I personally cannot subscribe to Dr. Theis' theory that the borax pushes acid ahead of it, but we are entitled to our theories about these things.

I think, if the acid is being pushed to the center, there should not be a sudden jump between one percent borax and one and a quarter per cent borax. If it is a general trend, it should start in the beginning. Of course, we know these experiments are on a practical scale and there is always a variation from skin to skin and pack to pack.

I wonder, Dr. Theis, if there might be some variation in these results caused by the fact that the center section is analyzed as a thicker slab than the thinner layers on the sides of the pieces? You are analyzing in one case a thin strip and in another case a thicker slab.

I would like to hear Dr. Theis on that point.

THEIS: I don't believe that the analysis is affected by the thinner center portion, due to the fact that the whole layers from the very same skins were put together and were allowed to air dry. The reason for splitting, of course, was to stop all diffusion at the time of neutralization. After the layers were air dried, they were ground into thin powder in the Wiley Mill, and there the analysis proceeded. So there should not be any difference in analytical area between the thicker middle section and any of the layers.

L. SELIGSBERGER: Did you do any experiments with ammonium hydroide? I think the explanation would be that ammonia displaces sulphuric acid, whether it is hydroxide or bicarbonate.

THEIS: All of the experiments, all of the anlytical work, was done from what you might call modification of the official method of our Association. We did not use ammonia.

H. B. MERRILL: I would like to ask Dr. Theis if the acid figures were the total acid as determined by phosphate displacement, or ammonia displacement method, or the protein-bound acid, as determined by water displacement and titration?

THEIS: The same way you devised it in 1926.

MERRILL: I did not devise this method. Gustavson, in 1926, published a method for distinguishing between protein-bound acid and chromium-bound acid, which simply involved immersing the leather in water and adding alkali to bring the solution to a pH value of about 5, and keep it there.

Later Gustavson published a different method using pyridine as a displacing agent, and all I did was to show that his first method was roughly accurate and his second method was erroneous in my opinion.

I take it, then, that you did not determine the total sulfate still combined with the chromium?

THEIS: Not for those charts. This is the total protein-bound acid.

MERRILL: Since the chromium-bound acid is greatly in excess of any protein-bound acid that may be there, it is quite possible that the neutralizing agent also reduced the chromium-bound acid to a considerable extent and that possibly some of these weird effects would become understandable, if we knew how much of the total displaceable sulphate had been removed. Regarding the alleged difference between ammonium bicarbonate and borax as neutralizing agents, we have run on a plant scale using ammonium bicarbonate, and we have run on a plant scale using borax as a neutralizing agent, and we found no difference whatever in the leather.

SOMMERVILLE: One point to remember is that half an hour of drumming may show a different result from that when the stock is later horsed up. It reaches an equilibrium later.

MERRILL: We have not determined protein-bound acid, either in the layers or the whole leather. Naturally, our neutralization was followed by dyeing, in which some acid was used, and fatliquoring. But the net result, as far as the whole leather was concerned, was that there was no difference in basicity and no difference in the temper of the stock or appearance of the grain, whether we used borax or ammonium bicarbonate (in equivalent amounts).

PETER R. BUECHLER: I should like to speculate about the nature of the process which Dr. Theis has described as a "pushing-in" of the acid toward the center of the skin.

If we look at the figure, 1-2, — and look also at the pH values listed, we see that the apparent migration of acid is not affecting the pH of the leather. Dr. Theis attributes this, I believe, to the fact that he is measuring hydrogen ion activity, and not hydrogen ion concentration as such. My personal belief is that as neutralization occurs at the surface of the leather, sodium sulfate is formed. Sodium sulfate will tend to be held to protein by dipole-ion interaction. The more acid your protein, the higher is the dipole effect. In the center of the skin, an acid condition still prevails. Consequently, sodium sulfate will tend to migrate into that area, and the salt ions will be held by interaction with the dipoles of the skin proteins. Such a bond would exert sufficient force to prevent the determination of this sodium sulfate by the

A.L.C.A. solubilization procedure for Neutral Sulfates. Hence, it would be classed as combined Acid Sulfate, which it is not.

THEIS: This is in answer to Dr. Merrill: His experience is entirely different from mine.

With ammonium bicarbonate we have usually had much softer leather than we have had with either sodium bicarbonate or borax. But every man's experience is his own, and if in Racine they get the same results, there must have been something different than you might get in Milwaukee or elsewhere. It is only a matter of interpretation.

It is very true, as Dr. Merrill says, that normally we go on from that operation. We neutralize and then we add our dyes and on top of the dyes, we add the fatliquor. The reason our experiments were taken at that point was we wanted to know something of the conditions obtaining just before the dyes were put on, because that is a condition that is going to affect your dyeing, whether it is bright or brilliant or dull. It is also going to have some effect on the up-take of the fatliquor. We are proceeding from that point to find out other things beyond the neutralization and this is only the preliminary paper.

The Sampling of Side Upper Leather

by C. W. MANN, E. B. RANDALL, JOHN MANDEL, T. J. KILDUFF, and A. M. CHARLES

1. INTRODUCTION

Some two years ago the Office of the Quartermaster General initiated a study of variables in tanning processes. Leathers were produced ranging from low to high chrome content and from no vegetable tannin to a high degree of retannage. The evaluation of these various lots* of leather by means of tests of their physical and chemical properties presented the usual difficulty encountered in leather testing. The large variability of these properties over the area of a side and among different sides might obscure the real effects due to changes in the tanning process. Since some of these effects were expected to be rather small, it became especially important, in this program, to devise a procedure for the sampling of the lots, that would insure a high probability of detecting differences between lots from the results of a reasonably small number of tests on each physical and chemical property. Consequently, the Advisors of the Office of the Quartermaster General recommended that a preliminary statistical study be made with the purpose of developing a sampling procedure that would meet these requirements. It was also recom-

*The word "lot" in specification language refers to a collection of hides or sides submitted in the same delivery and such that after an examination of a portion of it, the lot is accepted or rejected in its entirelty. In this paper the word "lot" will also be used to designate a collection of hides or sides obtained by a single tanning process in which all the variables were controlled.

mended that, if necessary, an extensive testing program be conducted on one lot of sides especially reserved for that purpose, to secure the data required for such a statistical study.

In addition to its value in solving the problem described above the information furnished by this study is needed as a basis for sampling leather for other research, for specification purposes and for general testing as in plant control.

II. Plan of Experiment

The main problems to be solved by the statistical study were:

(1) The selection, for each property, of an appropriate test specimen location.

(2) The determination of the number of sides in the sample*, necessary to insure the desired reliability for the evaluation of each characteristic of the lot.

(3) The determination of the required number of specimens to be tested on each side.

It soon became apparent that the problem of selecting the specimen location, appropriate for any given test, required for its solution, the formulation of a criterion by which the merits of different locations could be compared. This part of the task, while being essentially of a theoretical nature, nevertheless required the availability of a substantial body of reliable experimental data for each of the properties considered. A search of the literature failed to disclose information of this type that was of sufficient scope for the present purpose. Therefore an experiment was designed, in which a number of sides were to be entirely cut into test specimens for the various properties.

It was decided to use straight chrome tanned and stuffed steerhide, comparable in general to the retanned upper leather specified for the present Army service footwear. Chrome tanned leather of medium chrome and grease contents, split to 5.5 ounce weight, was selected as reasonably representative of the series of experimental leathers under investigation. A test is in progress now in which chrome-vegetable retan leather is being studied to check the applicability of the sampling procedure to this type of leather.

On the basis of information reported by Beek and Hobbs [1, 2] a lot size of 30 sides was considered adequate and was adopted for this experiment. The physical and chemical tests selected for the study were those generally applicable to shoe upper leather, i.e., tensile strength, elongation, stitch tearing strength, tongue tearing strength, bursting strength, density, water penetration, water vapor permeability, chromic oxide, hide substance, and grease. Considerations based on the required specimen sizes for the various tests as well as on the total area of the side for the selected stock led to the adoption

*The word "sample" is used, throughout this paper, with its usual statistical connotation; i. e., a collection of hides or sides, drawn at random from the lot, for the purpose of inspection and test.

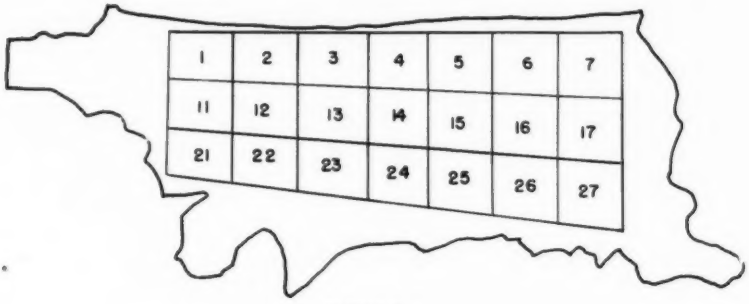


FIGURE 1.

of a pattern of 21 blocks or positions on each side, formed by three rows and seven columns, as indicated in figure 1. Specimens for most of the tests were to be cut from each block of each of the 30 sides. In order to reduce the size of the test blocks, bursting strength and water resistance specimens were to be cut from alternate blocks only. Figure 2 shows the pattern according to which each block was cut into specimens for the various tests. It will be noticed that for all strength tests, in which a directional effect may be expected, specimens were cut in two directions, parallel and perpendicular to the backbone.

III. Test Methods

The test methods used are described in Federal Specification KK-L-311 with a few exceptions. Water penetration was measured by the dynamic method developed by Maeser [3]. The strength tests, tensile, stitch tear, tongue tear, and burst were made on a Tinius Olsen Testing machine [4] which, by proper adjustment of the loading range, afforded a high degree of accuracy at any required load. A special adapter was developed for use with this machine for measuring bursting strength. This apparatus was used instead of the standard Mullen tester because the latter did not have high enough capacity to break all of the side leather specimens in this experiment. The adapter is shown in figure 3. Water vapor permeability was measured by the method developed by Kanagy and Vickers [5].

IV. Test Results

The results of the test for the various properties are summarized in table 1. The importance of the effect of the location from which a test specimen is cut on the value obtained is quite apparent, and becomes particularly evident when the "position range" is compared to the "range of side average." The range of position averages encompasses 21 values while that of side averages encompasses 30 values. Therefore, one would expect the range of side averages

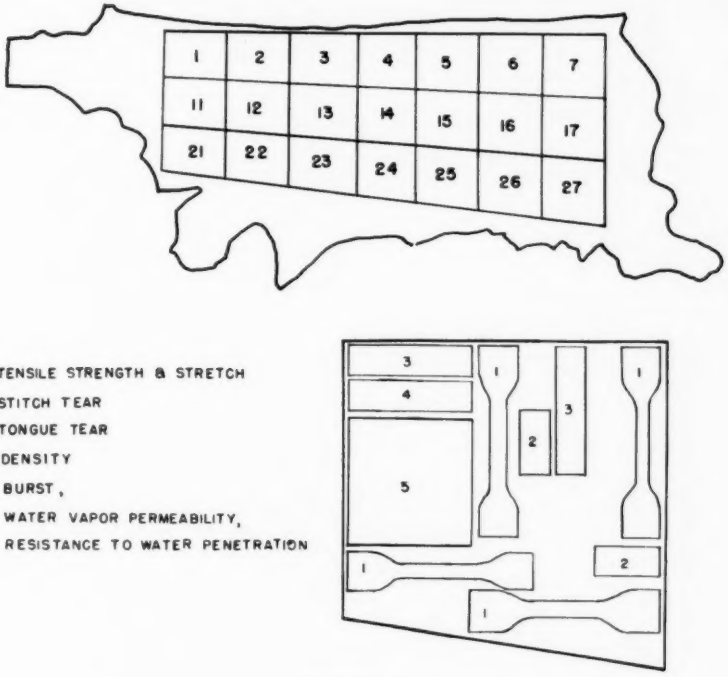
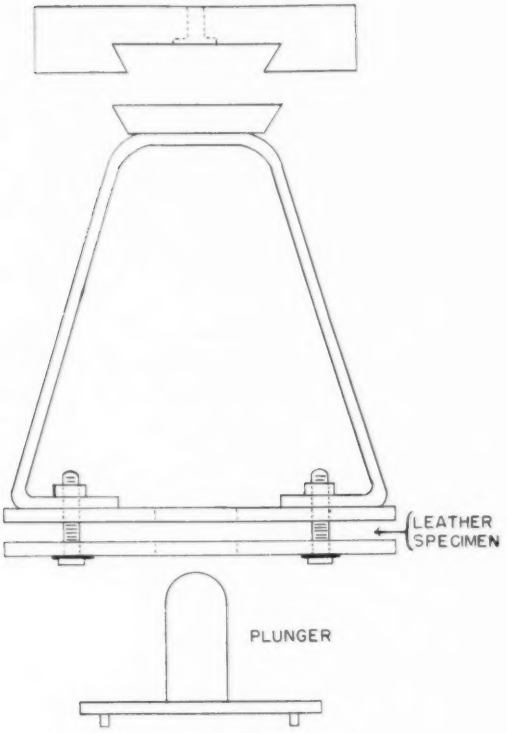


FIGURE 2.

to exceed* that of position averages, if the differences between positions were of the same order of magnitude as those between sides. The data at the bottom of table 1 show, however, that in the majority of cases, the range of positions is appreciably larger than that of side averages. This leads to the conclusion that the variation from one position to another on a given side is, in general, much larger than the variation from one side to another. This fact provides a justification for the common practice among research workers to compare treated and untreated leather in corresponding positions on different sides. By this procedure the experimental error is smaller than it would be if different positions from the same side were used in the comparison.

For a particular test, namely tensile strength, the position effect is illustrated graphically in figure 4. This figure reveals a pattern of variation of the property over the surface of the side, both in the parallel and the perpendicular direction with respect to the backbone. It also shows the marked difference

*By about 30 per cent in this case.



TEMPLATE FOR BURST TESTS
FIGURE 3.

between tensile strength when measured on specimens parallel to the backbone and the same property on specimens in the perpendicular direction. Incidentally, this circumstance reveals the fallacy of comparing leathers on the basis of tensile measurements made on sample pieces on which the direction is not properly indicated.

The sampling position specified for physical tests in both the Federal Specifications and the Official Methods of the American Leather Chemists Association corresponds approximately with position 6 of figure 1. Examination of table 1 shows that specimens cut from a block in that position will tend to give test results below the lot averages for tensile strength, bursting strength, stitch tear strength, and tongue tear strength.

V. The Sampling Problem

If in practice all 21 positions, i.e., the entire side, could be tested, it would be reasonable to characterize the side by the average of the 21 results obtain-

TABLE I

Position Averages for 30 sides

Position*	Physical Tests: Tensile strength, Parallel lb./in.²	Tensile strength, Perpendicular lb./in.²	Elongation at load of 100 lb./in. width, Parallel Per cent	Elongation at load of 100 lb./in. width, Perpendicular Percent	Bursting strength** 100 lb./in. thickness	Stitch tear, Parallel lb./in. thickness	Stitch tear, Perpendicular lb./in. thickness	Tongue tear, Parallel lb./in. thickness	Tongue tear, Perpendicular lb./in. thicknesss	Density g/cm³	Permeability to ‡ water vapor mg/25cm²/100 min	Water penetration‡ g/15 min	Chemical tests (dry basis)‡: Grease Per cent	Hide substance Per cent	Chromic oxide Per cent
1	5710	3040	8.9	52.8	135	1520	1060	440	540	.840	46	8.9	35.4	53.7	3.49
2	5400	3280	12.3	37.2	127	1440	1140	420	520	.814	52	7.3	33.0	56.6	3.56
3	5750	3720	17.3	30.5	120	1300	1120	410	600	.794	61	10.6	27.6	61.9	3.76
4	5020	3450	25.8	33.0	123	1290	1120	460	560	.794	70	8.1	26.4	62.8	3.90
5	5240	3310	23.8	35.0	123	1170	1010	440	530	.795	66	6.9	25.0	63.9	4.09
6	4200	2950	28.4	34.2	127	1040	950	400	410	.775	88	7.0	24.0	64.5	4.19
7	2760	3880	34.9	28.2	84	920	1040	420	530	.790	119	6.2	22.5	65.7	4.28
11	3740	4200	13.7	27.5	158	1690	1370	880	890	.861	33	5.3	36.4	53.1	3.51
12	5090	5100	13.8	23.8	148	1740	1640	820	860	.860	37	6.0	33.9	55.7	3.52
13	6620	5140	15.7	19.5	172	1370	1400	730	800	.820	39	5.1	29.5	60.0	3.69
14	6290	4410	11.5	24.0	143	1360	1360	620	700	.808	58	4.5	27.0	61.6	3.77
15	6610	4520	19.1	23.5	149	1390	1320	580	680	.814	64	3.8	27.0	62.1	3.93
16	4610	3860	23.2	23.8	138	1180	1160	510	460	.795	81	3.1	25.2	63.4	4.26
17	4650	4100	21.3	28.9	101	1330	1060	430	460	.767	118	4.9	26.1	61.9	4.10
21	2170	2920	57.5	42.8	129	1420	1240	830	810	.882	27	2.6	44.7	45.4	3.09
22	4400	3670	23.7	36.1	144	1490	1460	880	920	.883	40	3.1	44.0	45.7	3.10
23	3570	5880	32.6	25.0	164	1590	1590	910	840	.831	31	2.8	36.8	53.2	3.35
24	7310	5510	13.1	29.0	176	1490	1380	770	850	.823	52	3.8	30.3	59.0	3.59
25	7510	5280	13.9	32.7	169	1730	1360	810	890	.816	58	3.0	30.2	58.3	3.68
26	3670	4290	34.5	33.8	171	1740	1360	740	700	.825	40	4.0	38.2	50.6	3.42
27	4830	4730	21.6	29.7	140	1270	1330	680	740	.836	56	6.8	33.4	54.7	3.68
Position maximum	7510	5880	57.5	52.8	176	1740	1640	910	920	.883	119	10.6	44.7	65.7	4.28
Position minimum	2170	2920	8.9	19.5	84	920	950	410	410	.767	27	2.6	22.5	45.4	3.09
Position range	5340	2960	48.6	33.3	92	820	690	500	510	.116	92	8.0	22.2	20.3	1.19
Maximum side average**	5820	4810	26.0	38.3	164	1550	1400	790	840	.856	93	9.2	35.0	62.4	3.97
Minimum side average**	4200	3440	19.5	25.6	113	1160	1090	500	530	.739	44	2.3	26.3	54.6	3.42
Range of side average**	1620	1370	6.5	12.7	51	390	310	290	310	.117	49	6.9	8.7	7.8	0.55
Lot average†	5010	4160	22.3	31.0	140	1400	1260	630	680	.820	59	5.4	30.8	57.8	3.71

*The positions are denoted as in figure 1.
**These data were calculated from the individual test values (not given in this table); Each side average is the average of the 21 position values for that particular side.
†Average of the 30 side averages for the indicated property.
‡For this test, each position average is based on 15 test values instead of 30.

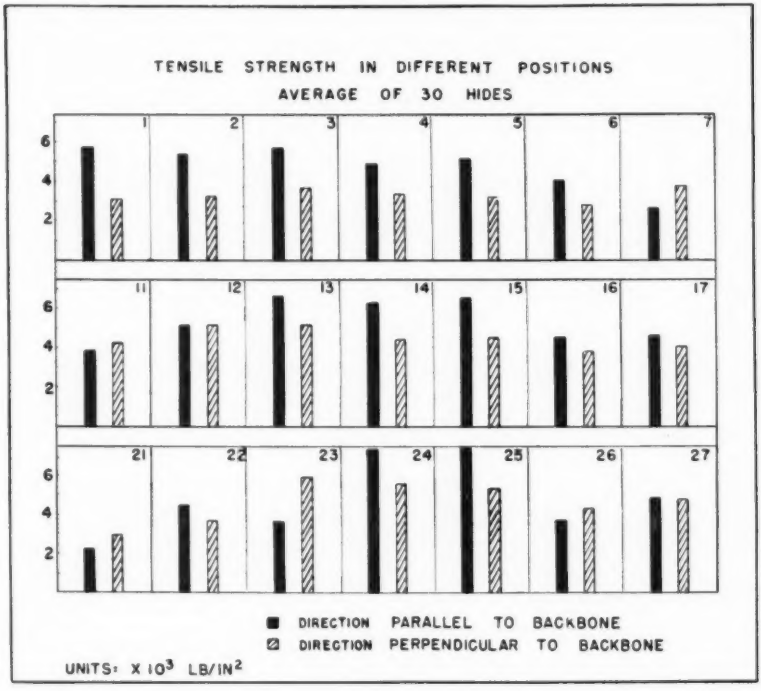


FIGURE 4.

ed. Such an average will be denoted in this paper by "h" and referred to as "side average." Then the average of a set of h-values, corresponding to a random sample of sides from a given lot is a reasonable measure of the value, characterizing the lot, for the characteristic under consideration. Because of the destructive nature of most tests it is generally impractical to cover the entire side. Thus arises the problem of finding a suitable "sampling location," i.e., a location from which test specimens for a particular property are to be cut.

The discussion in the preceding section, based on an examination of the data in table 1 and a study of figure 2 has already revealed the need for a judicious choice of a sampling location for each physical and chemical property. For some of the properties the direction of test as well as the location should be specified. It is also apparent that the problem must be examined for each property individually. It has already been indicated that the determination of the suitability of a particular position as a sampling location for a given test requires a criterion for the quantitative comparison of differ-

ent locations. It would be incorrect to base this criterion on the requirement that for a suitable sampling location the test result should be identical with the side average. As stated previously, two conditions must be fulfilled by a sampling location. It should furnish test results that will allow the detection of relatively small differences between lots, and this should be accomplished on the basis of tests on the smallest possible number of sides.

Of fundamental importance, for the solution of this problem, is the determination of the relationship between the test result in a particular location P—such a result will be noted by the letter p—and the corresponding side average h. This relationship cannot be inferred from the data in table 1, which only reveal relations between averages. One might assume that, for a given property, the value p, for any particular position P, must differ from the side average h by an amount nearly the same for all sides. Another plausible assumption would be to consider that p and h must, for a given position P, be in approximately the same ratio from one side to another. A more general assumption, containing the two previous ones as special cases, is the

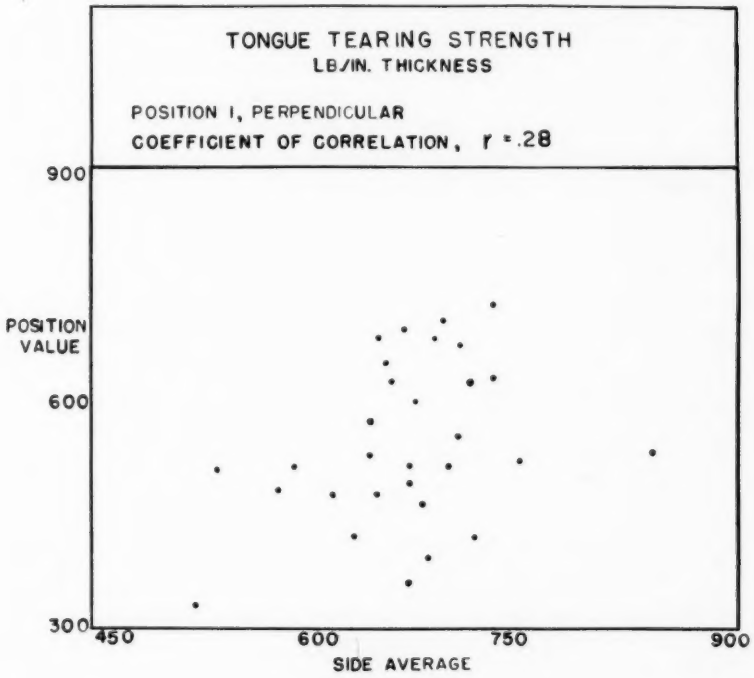


FIGURE 5.

existence of a linear relationship between p and h. In this case, a plot of p values versus the corresponding h values would approximate a straight line. Only an examination of the individual measurements can tell which of these assumptions, if any, is actually valid. Such a study was made and led to the conclusion that the results, for the various properties and locations, fall into two general classes. One class contains those cases for which no relation whatever can be observed between the individual p and h values. In this case the plot of p versus h shows a mere random scattering of points in the p, h plane. Figure 5, obtained from tongue tear data in position 1 is typical for this situation. The other class contains those cases in which the linear trend, i.e., a straight-line relationship between p and h, is readily discerned. Figure 6, illustrating tongue tear data in position 12, is typical for this class. Of course, there always exists some scatter of the experimental points even where a definite linear trend exists. It is also noteworthy that in the cases in which the linear trend was definitely found to exist, the straight line did not, in general, pass through the origin. Therefore, the assumption of a constant ratio between p and h is in general not justified.

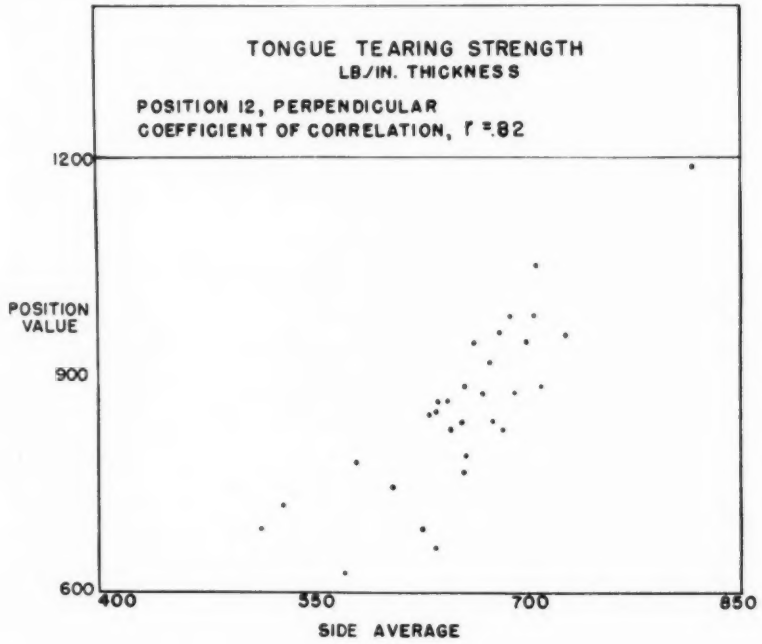


FIGURE 6.

On intuitive grounds it is now possible to set down conditions for a suitable sampling location:

a. Positions for which no relation between p and h exists are unsuitable, since the test specimen, bearing no relation to the side average, cannot possibly represent the side in any way.

b. Among the positions for which a linear trend exists, that one is to be preferred for which the slope of the p versus h line is relatively large. The reason for this is apparent on figure 7. The slope is the ratio of an increment of p, $\triangle p$, to the corresponding increment of h, $\triangle h$. A position P for which the slope is large corresponds to a situation in which a relatively small difference between sides will result in a relatively large difference between position values. This means that test specimens in that position are sensitive to side differences. This higher sensitivity will result in greater economy in sampling.

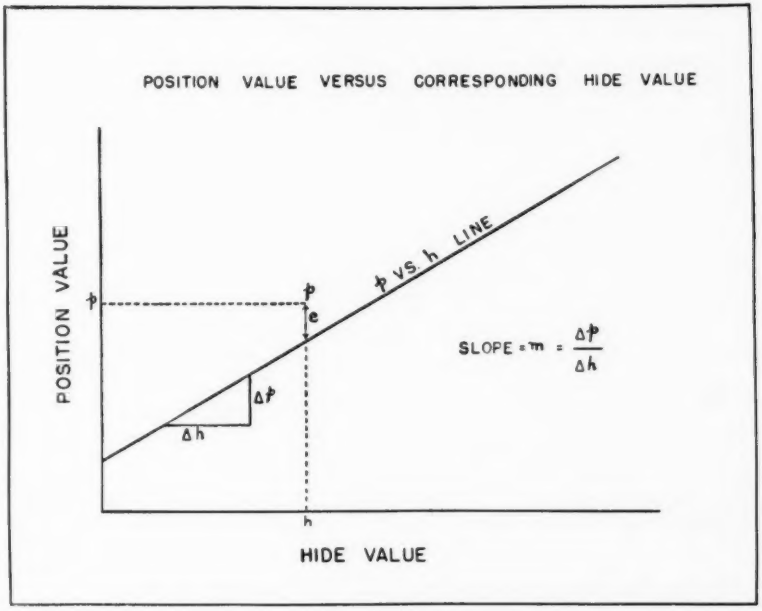


FIGURE 7.

c. The scatter of the experimental points around the straight line should preferably be small. In figure 7, p is an experimental point; its vertical distance e from the straight line is a measure of the degree of failure of this point to be exactly on the line. If the points scatter widely about the line,

the values e will, on the average, tend to be large. Naturally, a large amount of scatter will tend to reduce the effectiveness with which p represents h and consequently also reduce the suitability, as a sampling location, of the position P that gave rise to this set of points.

Since it is desirable that for a good position, m should be large and e small, it is seen that the ratio m/e should be large. It can be shown*, by statistical considerations, that this is indeed the criterion to be used for the selection of the most suitable sampling position for any particular property. In fact, a more convenient measure is used, known as the coefficient of correlation, r, which mathematically is closely associated with the ratio m/e and is large for large values of this ratio. Thus the most suitable sampling position, for a given property, is that in which the coefficient of correlation, r, for position and side values is largest.

The true value of the coefficient of correlation can only be determined on the basis of a very large number of experimental points, each corresponding to a side, since it requires that both m and the average value of e be known with complete accuracy. In practice, an approximation for this value is computed on the basis of test results from a limited number of sides. Such an approximation, known as "sample-estimate", is satisfactory provided that the number of sides is sufficiently large. The smaller the number of avilable points, the more uncertainty or "sampling-error" will be associated with the sample estimate r.

TABLE II

Grouping of Coefficients of correlation

Group	Range of r	
	Lower limit	Upper limit
0	0.94	1.00
1	.91	.94
2	.85	.90
3	.75	.84
4	.61	.74
5	.46	.60
6	0	.45

This raises the question regarding the precision with which the true coefficient of correlation can be estimated on the basis of the test results from the 30 sides available in this experiment. Figure 8 shows for every value of r calculated from 30 sides, the upper and the lower limits of the interval in which the true coefficient can be said to lie with 80 per cent confidence. It is seen that the precision of high observed values is considerably better than

*The statistical theory for the sampling problem with which this paper is concerned is given in another publication, appearing in the Journal of Research of the NBS.

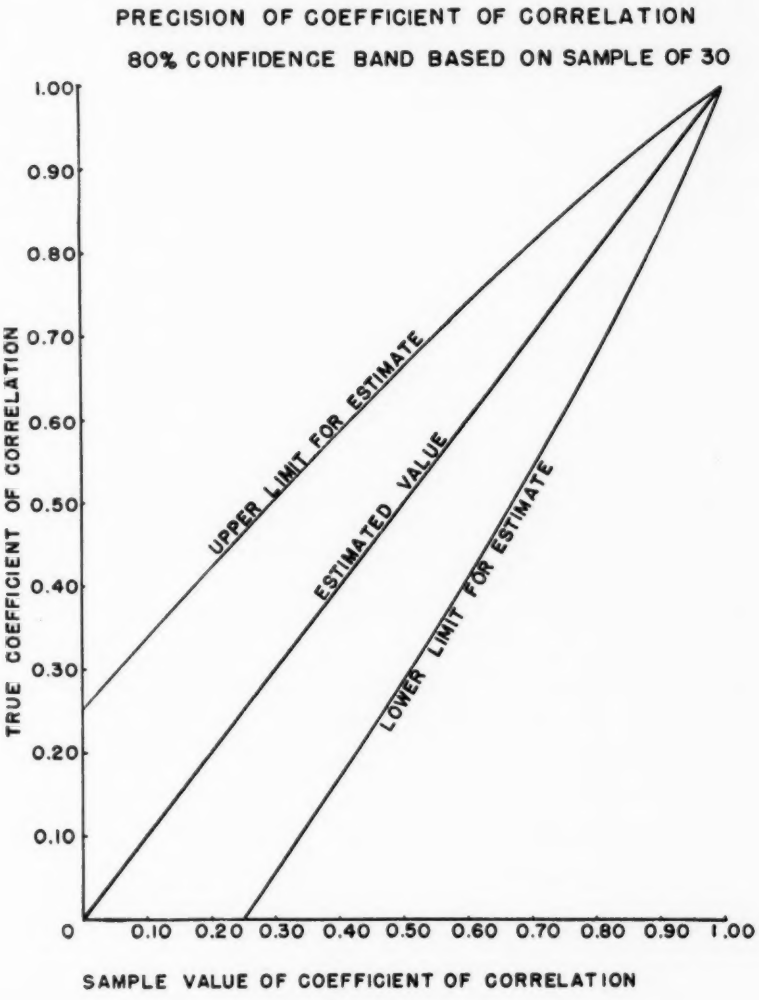


FIGURE 8.

that of low observed values. In view of these facts, small differences in r values, and, for the lower ranges, even moderate differences, may not reflect a real difference between positions. Therefore, a grouping procedure was adopted by means of which positions showing slightly different r values are

included in the same group†. The application of this procedure leads to a high probability to classify a particular position either where it belongs, or, at worst, in one of the two adjacent groups.

In the grouping of the positions on the basis of r values it was found that no value greater than 0.94 was obtained in any test. Therefore, the interval in r values from 0.94 to 1.00 was designated as group zero. The ranges of r values for each of the groups considered are given in table 2. It will be observed that the intervals widen as r decreases as would be expected from the corresponding decrease in precision of observed r values as they approach zero.

The grouping of the side positions for sampling purposes is given in table 3. The lower the group number for a particular property in a given position, the more suitable will that position be as a sampling location for this property, in the sense that a smaller number of sides will be required as a sample for such locations. A dash (—) indicates an unacceptable position for the property considered, since for this group the existence of any correlation between position value and side average is doubtful.

It is obvious that the selection of the most suitable sampling location does not, in itself, insure that the lot will be adequately represented by the sample. Thus, even total sampling of the side, i. e., testing of all 21 locations will be unsatisfactory if it is done on an insufficient number of sides or on a sample of sides not taken at random from the lot. The additional factor here involved is the variability between sides of the same lot, and any reasonable sampling procedure must take this factor in account. The procedure outlined in this paper for the selection of the most suitable sampling location will yield that location on the side for which the smallest number of sample sides is required from a lot of given side-to-side variability. What that number of sides will be depends, of course, on the variability between sides in the lot, as well as on the characteristics of the selected sampling location. In table 4, the side-to-side variability observed on the lot of 30 sides used in this experiment is given for each property, in terms of per cent coefficient of variation*. In the following section a formula is given for the calculation of the number of sides required under any given set of conditions.

VI. Calculation of Sample Size

If two lots are to be compared for a particular property, it is important to know how many sides should be taken from each lot, in order to detect, with a given degree of confidence, the minimum difference in which one is interested

†The grouping problem is somewhat complicated by the dependence of the precision of r on its magnitude. Therefore the r-values were subjected to "Fisher's z-transformation" (cf. ref. 5) prior to grouping. The z-values obtained by means of this transformation have a practically uniform precision over the entire range of variation of the correlation coefficient.

*The coefficient of variation is the ratio of the standard deviation to the average value. It therefore represents a measure of the variability of a quantity, expressed as a fraction of the magnitude of this quantity. Often, as in this case, the coefficient of variation is multiplied by 100, and then represents a percentage variation.

TABLE III

Group ranking of side positions for sampling purposes*

Physical tests	Side position																						
	1	2	3	4	5	6	7	11	12	13	14	15	16	17	21	22	23	24	25	26	27
Tensile strength,																					
Parallel	4	5	4	4	4	4	5	–	–	–	5	5	4	4	–	–	–	5	–	–	–
Perpendicular	–	–	5	–	4	5	5	4	5	–	–	4	4	3	–	–	5	5	5	5	4
Elongation,																					
Parallel	–	5	–	5	4	4	5	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Perpendicular	–	–	5	–	–	4	4	5	–	5	5	–	5	4	–	–	–	5	5	–	–
Bursting strength	4	5	5	–	4	–	4	5	5	4	3	3	4	4	–	4	–	–	5	–	5
Stitch tear,																					
Parallel	5	4	5	–	5	5	5	–	4	–	4	–	–	–	–	–	5	–	–	5	5
Perpendicular	4	4	–	–	–	5	5	4	4	–	4	–	–	–	–	–	4	5	–	5	–
Tongue tear,																					
Parallel	5	–	–	–	5	5	4	4	3	4	5	4	5	4	5	4	5	5	5	5	4
Perpendicular	–	5	–	–	4	4	5	4	3	–	5	–	3	5	–	4	4	3	–	5	5
Density	2	2	2	1	2	2	1	–	–	1	2	2	1	2	–	–	3	2	3	4	4
Water vapor permeability	4	2	5	2	5	3	2	–	5	4	3	3	3	3	–	3	4	3	3	5	3
Water penetration	4	4	5	2	5	3	4	5	1	–	–	4	4	3	–	–	–	4	–	5	5
Chemical tests																					
Chromic oxide	5	4	3	2	3	4	4	5	4	3	4	2	3	3	3	4	3	2	4	3	2
Hide substance	–	–	4	5	3	4	3	5	4	–	–	4	4	3	3	4	3	4	5	4	4
Grease	4	5	3	4	3	4	2	5	3	–	4	4	3	3	2	3	2	4	2	4	3

*A dash (–) indicates an unsatisfactory sampling position.

with regard to this property. It is assumed that the property is measured, on each side, in the same position P, for which the coefficient of correlation is known to be r. Suppose that it is required to detect a minimum difference of D per cent with respect to this property. It can then be shown that the number of sides, N, that should be tested in each lot, is given by the formula

$$N = K\frac{V^2}{r^2D^2}$$

where V is the coefficient of variation, in per cent, characterizing the side-to-side variability within each lot for the property under consideration. The factor K depends on the degree of confidence required for the detection of D.

It was pointed out previously that two specimens per location on the same side were tested for some of the properties. An analysis of the data showed that in general the difference between such duplicates was small as compared

TABLE IV

Side-to-side variability within the lot*

Properties	V Per Cent
Physical	
Tensile strength	7.8
Elongation	5.4
Stitch tearing strength	5.8
Tongue tearing strength	8.9
Bursting strength	7.6
Density	2.8
Water penetration	27.1
Water vapor permeability	24.3
Chemical	
Hide substance	3.0
Grease	6.2
Chromic oxide	3.7

*The values given in the table are per cent coefficient of variation, i. e., standard deviations expressed as per cent of the lot average value.

to the variability of results between different sides or different positions. Therefore, there is little advantage in testing, for each property, more than one specimen per side, on the location selected for that property.

It is possible that a considerable improvement could be obtained by sampling from more than one location for each property. No investigation of this point has been attempted in this work, mainly because of the experimental disadvantages of such a procedure as well as for reasons of economy in the use of the limited supply of the leather in the experimental lots for which the sampling procedure was devised.

TABLE V.

Number of sides required for detection of D per cent difference between lots

D Difference to be detected	Confidence of detection* 90 Per Cent: Single position sampling Coefficient of Correlation 0.40 Sides	0.65 Sides	0.90 Sides	Total sampling** Sides	Specimens	95 Per Cent: Single position sampling Coefficient of correlation 0.40 Sides	0.65 Sides	0.90 Sides	Total sampling** Sides	Specimens
5	273	103	54	44	924	415	157	82	66	1386
10	68	26	13	11	231	103	40	20	16	336
15	30	11	6	5	105	46	17	9	7	147

*A precise definition of this term is given in the companion paper on the theory[1] (ref.1).

**Testing all 21 locations of each side in the samule. In this case the number of specimens equals 21 times the number of sides.

As an example for the application of the formula consider tensile strength measurements, for which the coefficient of variation of side averages (V) is about 8 per cent. Table 5 lists for this case the number of sides, N, to be taken from each lot, for detecting differences of 5, 10, or 15, per cent, using positions for which the coefficients of correlation are 0.40, 0.65, or 0.90. Evidently, the higher the confidence required the larger will be the sample necessary to detect D with that confidence. It will also be observed that the number of sides required increases rapidly as the difference D to be detected decreases from 15 to 5 per cent.

A striking illustration of the economy resulting from the selection of a good sampling position is obtained by comparing the number of specimens required for a position in which $r = 0.90$ to that of total sampling of the side. For example, the table shows that if a 10 per cent difference between lots is to be detected with 90 per cent confidence, sampling in the single position $r = 0.90$ requires 13 sides as compared to 11 sides if all 21 positions of each side are tested. In the first case only one specimen per side is required whereas in the latter case 21 specimens per side are required. Thus the numbers of specimens required in the two cases are in the ratio 13: (11 x 21) or 13: 231. This clearly shows the tremendous saving in both leather and labor resulting from the application of a good sampling procedure.

Based upon the results of this study, a sampling procedure was devised for Quartermaster experimental upper leather currently under investigation. In the selection of the sampling position for a particular test, consideration was first given to the highest ranking groups for that test. However, other factors were considered such as the desirability of grouping the test specimens in a small area in order to minimize the destruction of leather in other areas designated for storage and wear tests.

The results of this study have been made available to the American Leather Chemists Association Committee on Sampling, as a basis for the development of a standard sampling procedure for side upper leather.

Acknowledgments

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VIII. References

1. *J. Am. Leather Chem. Assoc.* **32,** 4 (1937).
2. *J. Am. Leather Chem. Assoc.* **36,** 190 (1941).
3. *J. Am. Leather Chem. Assoc.* **42,** 390 (1947).
4. ASTM Bulletin (Tinius Olsen Machine).
5. *J. Research N. B. S.* **45,** 2 (1951).

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Canaigre Investigations

Countercurrent Stationary Vat Leaching of Shredded Canaigre Roots

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INTRODUCTION

In recent years, there has been much interest in developing new domestic sources of vegetable tanning materials. The need for tannin in this country and the reasons for the decline in domestic production have been discussed rather thoroughly by Rogers and Russell [8]. In this Bureau emphasis has been placed on extraction of tannin from roots of canaigre (*Rumex hymenosepalus* Torr.), which grows wild in New Mexico, Arizona, Texas and California and which can be cultivated on marginal land. Tannin was extracted from canaigre on a commercial scale as early as the eighteen nineties [4] but because of economic problems and the difficulty of obtaining a steady supply of roots its commercial manufacture was discontinued.

When freshly dug, canaigre roots contain 65 to 75 per cent moisture. The tannin content* and purity (ratio of tannin to soluble solids†) depend on the strain and the conditions under which the plant is grown. On a dry basis the tannin content ranges from 20 to 35 per cent and the purity from 40 to 65. In general, strains with roots having reddish interiors seem to have the higher tannin contents and purities; therefore this strain was used for the experiments. The roots contain considerable starch—about 20 per cent on the dry basis.

In commercial practice, tannin is extracted from various barks and woods with hot water in open leach vats or in pressure autoclaves. Leaching canaigre roots, however, is complicated by the starch. To prevent swelling or gelatinization of the starch, which makes the tannin difficult to extract and the liquors practically impossible to clarify economically, comparatively low temperatures must be used. Also, as reported by Cordon, Beebe and Rogers [3], leaching canaigre shreds with water at 60 to 65° C. produced such a compact bed that the flow was seriously restricted and at lower temperatures tannin recovery was low. Beebe, Cordon and Rogers [2] employed a centrifugal filtration method of leaching finely comminuted particles of canaigre with water at 112° F. This procedure, however, necessitated the mechanical handling of solids as well as liquids between each leach, and this would be rather expensive in large-scale processing. Therefore, it was decided to attempt the leaching of large

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†Tannin and soluble solids contents were determined by extracting the roots with 50 per cent aqueous acetone by the method of Luvisi and Rogers (7), and analyzing the extracts by the official methods of the American Leather Chemists Association (1). These methods were followed in all analyses reported in this paper.

particles of canaigre in standard-type vats, leaving the solid material in the vat for successive leaches until it was completely spent and moving only the liquors progressively from one vat to another, and to use an aqueous solution of an organic solvent as the extractant. Luvisi, Cordon, Beebe and Rogers [6] reported laboratory-scale leaching of canaigre shreds in Reed-Churchill extraction tubes with a 50 per cent acetone-water solution. The present paper describes pilot - scale investigations made concurrently with those just mentioned. It includes studies on permeability of beds of commercial depth and adequate diameter and also investigations of countercurrent leaching of canaigre shreds with dilute aqueous solutions of isopropyl alcohol.

Preliminary Batch Studies on Solvents and Permeability

To determine the practicability of the leaching method, a single glass column 4 inches in diameter and 4 feet high was set up (Fig. 1). The liquor was circulated externally through a heating coil and rotameter by a centrifugal pump. The packed column of roots was supported by a false bottom of wire-mesh screen. To prevent contamination of the tannin liquors with iron, all parts of the apparatus coming in contact with the solution were made of copper, brass, or stainless steel. To avoid compaction of the bed of solids by suction, atmospheric pressure was maintained at the bottom of the column by throttling the flow rate of the pump.

To obtain a bed of canaigre roots that will remain permeable for extraction, the material must consist of uniform shreds with a minimum of fines. Several methods of preparing the fresh roots in such a form for drying were investigated. A sugar beet shredder, which has high capacity, produced material only about 75 per cent of which was shreds, and even these were nonuniform in cross section and contained many thin particles, which buckled and compacted in the leaching tanks. A Kummer shredder, which is relatively inexpensive, produced a material 80 per cent of which was held on an 8-mesh screen but again the shreds were nonuniform. The best method found for preparing uniform shreds was to use a vegetable dicer, which first cuts the roots into uniform slices and then shreds the slices with a set of revolving circular knives. This method produced a material of which 96 per cent was retained by a 7-mesh screen and which consisted of 91 per cent by weight of uniform cossettes $\frac{1}{8}$ inch square. Even though this material contained some fines, it did not require any screening and gave a permeable bed for solvent extraction.

In many cases, particularly with roots prepared on the Kummer shredder, the material was screened before extraction even in the small, 4-inch diameter column, because much of this material had been roughly handled, and a considerable amount of fines had been made accidentally. By screening the material, the permeability of the cossettes could be evaluated without interference from these accidental fines. Also when the small column was used,

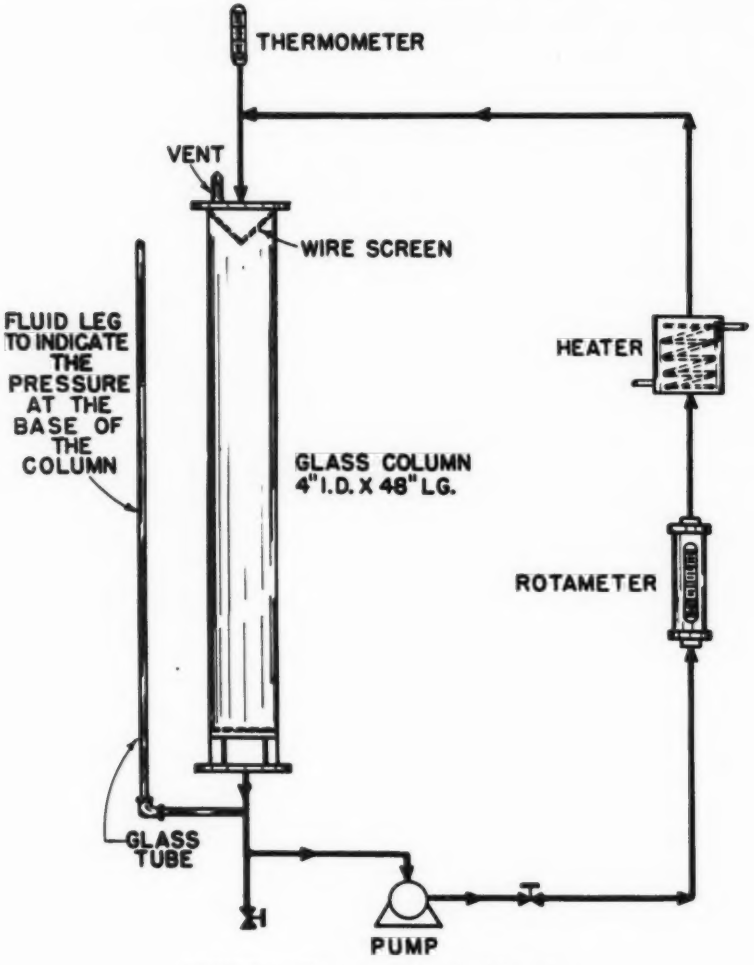

FIGURE 1—Diagram of 4-foot leaching column.

the dried roots were in many instances rehydrated and rechopped to eliminate wall effects. This rechopping would not be necessary in leaching vats of larger diameter.

A number of batch runs were made in which the roots were leached several times; fresh solvent was used for each leach. For one series the solvent was water at 112° F.; for another it was a 25 per cent by volume aqueous solution

of acetone at room temperature. Previous investigators had found that both are satisfactory extractants for canaigre tannin [6, 7]. They showed that the temperature of the acetone does not affect the degree of extraction. Acetone would be expected to give a better extraction, but it would increase the cost of processing per pound of raw material. Table I lists the results of these experiments.

Because of the hazard in using acetone and the expense that this hazard would entail, use of isopropyl alcohol was investigated. Small-scale laboratory tests showed that at room temperature, 25 per cent by volume of aqueous isopropyl alcohol extracts canaigre tannin better than warm water but not so efficiently as acetone. Increasing the temperature, however, appeared to increase the solubility of canaigre tannin in isopropyl alcohol solutions; 18 per cent isopropyl alcohol at 112° F. was as effective a solvent as 25 per cent. With acetone, 25 per cent seemed necessary for high extraction, and temperature had no effect. Accordingly, several runs were made with isopropyl alcohol in the small column. Table I also lists these results.

TABLE I

Batch Leaching of Canaigre in 4-Foot Column

Experiment No.	Solvent	Preparation of Roots	Temp., °F.	Number of Leaches	Total Ratio of Solvent-to-Solids	Cumulative Tannin Recovery, %
W12*	Water	Screened on a 7-mesh screen. Hydrated to 58% moisture. Re-screened on a 4-mesh screen	111	4	17	48
C1*	25% acetone	Ditto	83	4	13	81
W13	Water	Screened through a 2-mesh screen and on a 7-mesh screen. Hydrated to 59% moisture.	111	4	16	31
C3	25% acetone	Ditto	80	4	13	63
E3	18% isopropyl	Ditto	111	4	13	65
W14	Water	Screened through a 2-mesh screen and on a 7-mesh screen. Hydrated to 35% moisture. Ground in sharp-knife hammer mill with ½ inch screen. Rehydrated to 60% moisture.	112	7	24	50
C4	25% acetone	Ditto	85	7	21	75
C5	25% acetone	Ditto	79	7	19	71
E1	25% isopropyl	Ditto	79	7	20	62

*Roots used in experiments W12 and C1 were from the same lot; those used in the other experiments were from another lot.

From the first pair of experiments listed in Table I (W12 and C1), it can be seen that cold 25 per cent aqueous acetone gave much better extraction

than warm water even when less organic solvent was used. The solvent-to-solids ratio (ratio of total liquid used to original dry weight of solids) was 17 in the water experiment and 13 in the acetone experiment. In all these experiments (Table I), each leach was long enough to make the rate of change of concentration with time extremely small. This meant that in this batch work the first leaches required the longest times. In all the later batch experiments (except C1 and W12, in which all the leaching times were longer), the duration of the first leach was approximately 60 minutes, the second 40 minutes, and the third 30 minutes; and in all succeeding leaches it was 20 minutes. The second set of experiments (W13, C3 and E3) illustrated the same point, although the degree of extraction (recovery of tannin) was different for this lot of roots. They also showed that warm 18 per cent isopropyl alcohol was as good an extractant as the acetone. The third set of results (W14, C4, C5 and E1) again illustrated the increase in extraction with organic solvents and showed that cold 25 per cent isopropyl alcohol was better than warm water but not so good as 25 per cent acetone. The two 25 per cent acetone experiments (C4 and C5) show the effect of a lower solvent-to-solids ratio.

To test the permeability of beds of shredded canaigre of commercial depth, a new column 10 feet high and 9 inches in diameter was constructed (Fig. 2) similar to the 4-foot column. Two batch experiments were made with isopropyl alcohol and acetone under conditions comparable to those used for the experiments in the small column. The roots were shredded in a Kummer shredder with $\frac{1}{8}$ inch beet cossette knives before they were dried. After they were dried they were screened through a 2-mesh screen and on a 7-mesh screen. The results of these experiments (Table II) show that extraction in the large column was about the same as in the small column. The slight decrease in recovery in the isopropyl alcohol experiment in the large column was probably due to the lower alcohol concentration used in this run and the lower solvent-to-solids ratio. The permeability of the beds in both these runs was excellent, and by maintaining atmospheric pressure at the bottom of the column in the same way as in the small column, the resistance of the packing never required that the flow be lowered below 1.5 gallons per minute per square foot. The time required for free drainage of liquor over the 10-foot depth was approximately 10 minutes.

Later, an experiment was made with $\frac{1}{8}$ by $\frac{1}{8}$ inch shreds cut in an Urschel vegetable dicer before they were dried. No fines had to be discarded. With an 18 per cent by volume aqueous solution of isopropyl alcohol as the solvent, the lowest flow (after seven leaches) was 2.5 gallons per minute per square foot and the free drainage time was 10 minutes. With the same material and with water as the solvent, the bed quickly packed down and became almost impermeable. Therefore water was eliminated from consideration as a solvent for this method of extraction.

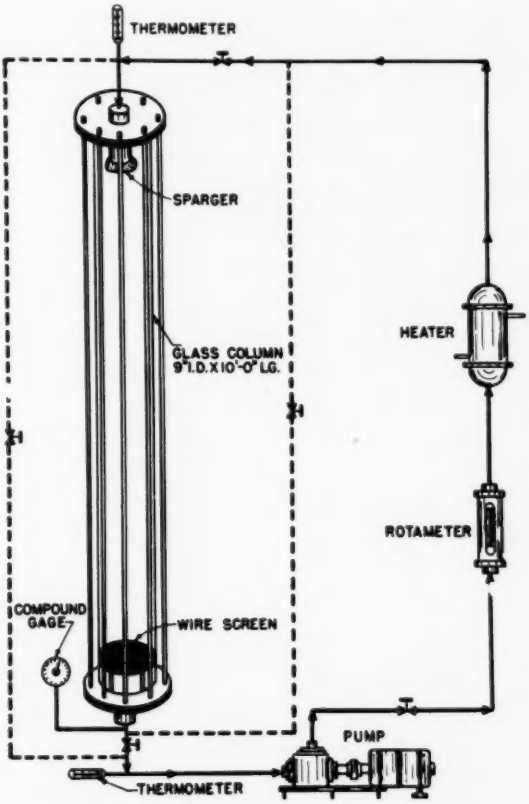

FIGURE 2—Diagram of 10-foot leaching column.

Countercurrent Leaching

To determine recoveries that could be expected in commercial countercurrent operation, a battery of four columns 4 feet deep was constructed (Fig. 3). By drawing off and holding the liquors and, if necessary, the roots, this battery could be used for countercurrent operation with any number of leaches. Figure 4 illustrates the procedure for starting this battery. A batch of roots is put into the first cell (A1, Fig. 4) and is extracted with fresh solvent. This liquor is then discarded. The second batch of fresh solvent is circulated over these partially spent roots (A2) and then over a batch of fresh roots (B1) and is then discarded. This procedure is followed until the required number of cells for the countercurrent extraction are in operation. Then the first

TABLE II

Comparison of Leaching in 4-Foot Column and 10-Foot Column

Experiment No.	Column	Solvent	Preparation of Roots	Temp. °F.	Number of Leaches	Total Ratio of Solvent-to-Solids	Cumulative Tannin Recovery, %
C5	Small	25% acetone	Screened through a 2-mesh screen and on a 7-mesh screen. Hydrated to 25% moisture. Ground in sharp-knife hammer mill with ½ inch screen. Rehydrated to 58% moisture.	79	5	14	65
C9	Large	25% acetone	Screened through a 2-mesh screen and on a 7-mesh screen. Hydrated to 58% moisture.	83	5	15	64
E3	Small	18% isopropyl	Screened through a 2-mesh screen and on a 7-mesh screen. Hydrated to 60% moisture.	111	6	19	72
E4	Large	16% isopropyl	Ditto	112	6	18	67

batch of roots, the most spent, (A6) is removed from the system, the fresh solvent is put on the next batch (B6), and a fresh batch of roots is put on the head end. The battery is run in this manner until the system reaches equilibrium, as indicated by the constancy of composition of the head liquors. Liquors from G1 or H1 are usually close to equilibrium. For tannin extraction, a quick indication of the composition of the head liquor can be obtained by density measurements.

Ten leaches was the largest number used in the countercurrent operation of this apparatus. During each leach, the liquor was circulated for 45 minutes before being transferred to the next batch of roots. The spent material, which had been leached 10 times, was discharged dripping wet and discarded. In commercial practice, the spent material would probably be pressed and the press liquor returned to the system with the fresh solvent. The canaigre used was screened on a 5-mesh screen and rehydrated to 57 per cent moisture with aqueous isopropyl alcohol. The solvent used was 18 per cent by volume aqueous isopropyl alcohol at 112° F.; the solvent-to-solids ratio was 9.2 to 1.

At equilibrium, the last three head liquors contained 81 per cent of the tannin in three batches of fresh roots (shown by analysis). The average tannin content of the last three batches of spent roots corresponded to 9 per cent of the tannin present in the fresh roots. Three liquors and three batches of spent roots were used to determine the recoveries to compensate as much as possible for mechanical losses or surges in the system. The total material balance showed 3 per cent loss, whereas the tannin balance showed a 10 per cent loss. Most of this loss was probably in the mechanical handling of the liquors and would not be nearly so large in large-scale operation. It

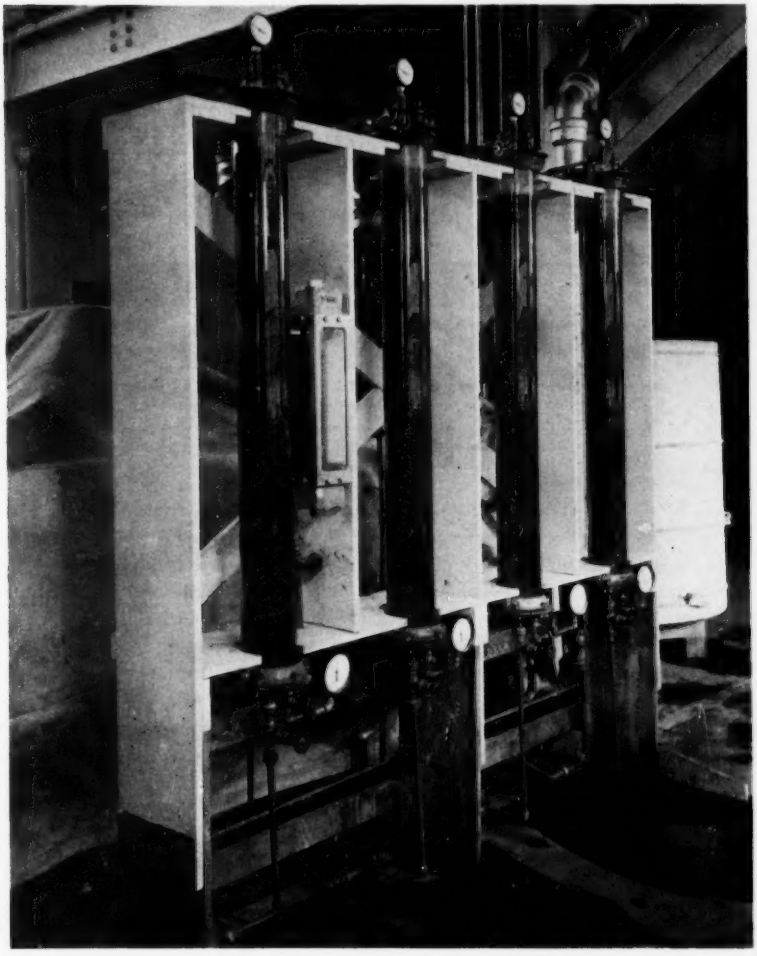

FIGURE 3—Countercurrent Leaching Battery.

is thought, therefore, that these results indicate a potential tannin recovery of somewhat higher than 81 per cent by this method on a commercial scale.

Samples were taken of the liquors in each cell of the battery at equilibrium and were analyzed for tannin content. The tannin recoveries calculated from these analyses are plotted in Figure 5. Also, at equilibrium 1-ounce samples

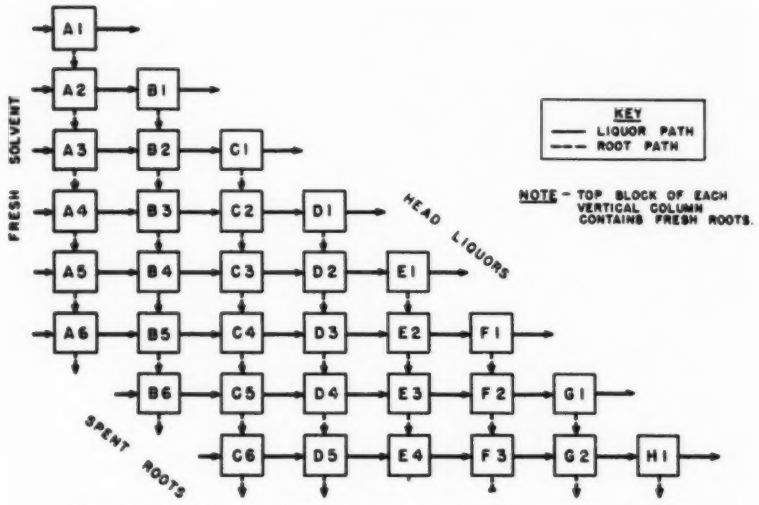

FIGURE 4—Diagram of Procedure for Starting Countercurrent Battery.

were taken in each cell every 5 minutes, and the specific gravity of these samples was measured with a pycnometer to show the approach to equilibrium in each cell. These values are plotted in Figure 6. The last three leaches show no increase in density after 15 minutes, indicating that the 45 minutes chosen for the time of leaching was considerably more than adequate.

The tannin recovery of 81 per cent obtained in this experiment with 10 cells and an 18 per cent solution of isopropyl alcohol shows some improvement over the value of 77 per cent reported by Luvisi *et al*[6] for a 15-cell leach with a 50 per cent solution of acetone. Also the work here reported with the large column indicates that packing and channeling can be avoided in commercial practice by proper shredding. However, both these recovery values are lower than the 90 to 93 per cent recovery obtained by Luvisi *et al*[6] with various solvents, a finer comminution of the roots, and use of a batch slurrying process.

Conclusions

These experiments showed that canaigre roots can be leached in beds of commercial depth without compaction of the bed and restriction of the flow of solvent if the roots are cut in uniform shreds and if a 25 per cent by volume aqueous solution of acetone or an 18 per cent solution of isopropyl alcohol is used as the solvent. The latter solvent is preferred because it is much less hazardous. In this work the roots were cut in a vegetable dicer to uniform

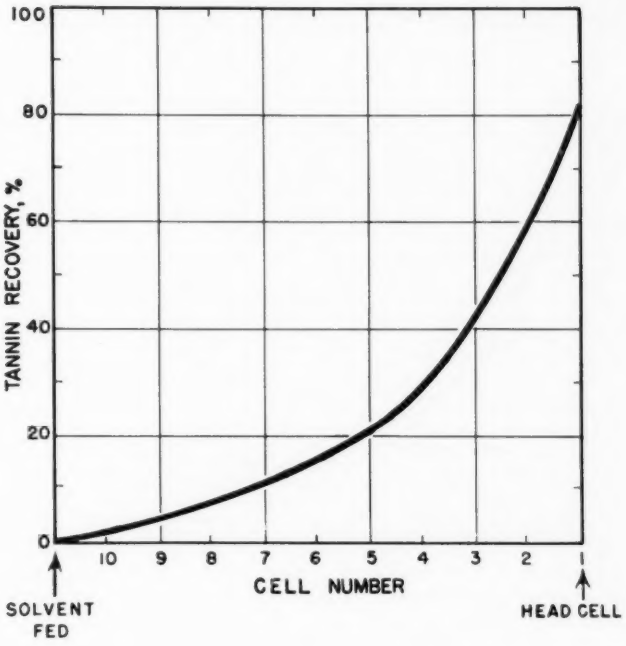

FIG. 5

TANNIN RECOVERY IN LIQUORS PASSING FROM EACH CELL OF 10-CELL BATTERY.

FIGURE 5—Tannin Recovery in Each Cell of a 10-Cell Battery at Equilibrium.

cossettes approximately $\frac{1}{8}$ inch square. With roots prepared in this form and a 10 cell stationary vat countercurrent system, a tannin recovery of 81 per cent has been obtained when an 18 per cent by volume aqueous solution of isopropyl alcohol is used as the solvent. Other methods of extraction now being investigated, however, seem to promise higher extraction efficiencies and lower costs per pound of finished tannin.

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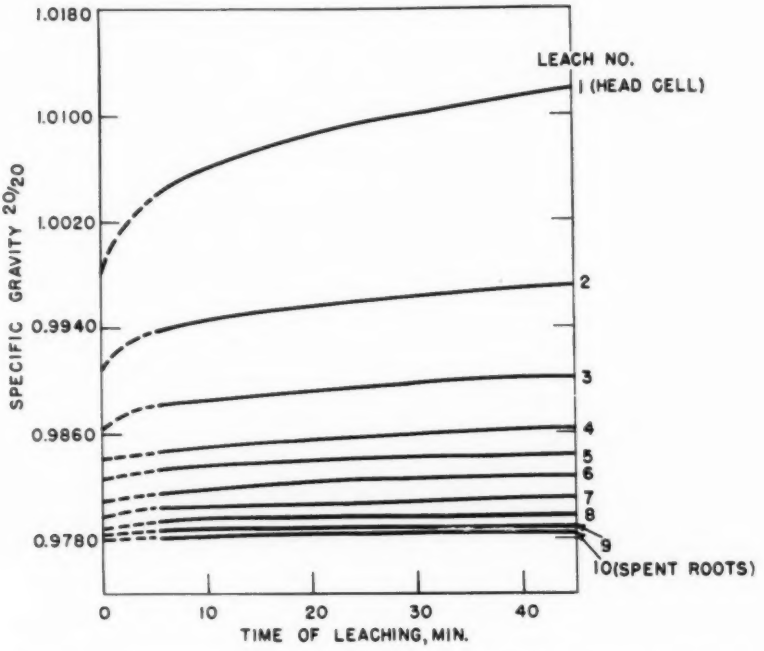

FIGURE 6.—Approach to Equilibrium in Each Cell of a 10-Cell Battery at Equilibrium.

Literature Cited

1. American Leather Chemists Association, Methods of Sampling and Analysis, 1943.
2. Beebe, C. W., Cordon, T. C., and Rogers, J. S., *J. Amer. Leather Chem. Assoc.*, **41**, 161 (1946).
3. Cordon, T. C., Beebe, C. W., and Rogers, J. S., *J. Amer. Leather Chem. Assoc.*, **42**, 118 (1947).
4. Gulley, F. A., *Agr. Sci.* **8**, Nos. 6–9, p. 320 (1894).
5. Kummer, F. A., "Equipment for Shredding Sweet Potatoes Prior to Drying for Livestock Feed", Circular 89, Agr. Expt. Station, Alabama Polytechnic Institute, June 1943.
6. Luvisi, F. P., Cordon, T. C., Beebe, C. W. and Rogers, J. S., *J. Amer. Leather Chem. Assoc.*, **44**, 707 (1949).
7. Luvisi, F. P., and Rogers, J. S., *J. Amer. Leather Chem. Assoc.*, **43**, 166 (1948).
8. Rogers, J. S., and Russell, G. A., *J. Amer. Leather Chem. Assoc.*, **39**, 467 (1944).

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Development of A Dynamic Stitch Tear Fatigue Test for Leather

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The development of test methods for leather and other fabrics should in every case simulate as nearly as possible the conditions encountered in the service of such material during actual wear or usage. When possible such conditions should be accelerated in the laboratory so as to give quick results which can be interpreted in terms of service.

Stitch tear resistance is a most important quality in all fabrics which are sewn. Until now a more or less static type of test has been used such as in the A.L.C.A. Methods of Testing and Analysis and U. S. Federal Specification KK-L-3-11. The results of such a static test being interpolated as a straight line function from $^1/_{16}$ to 1 inch in thickness is unsound in such a heterogeneous material as leather. No sound or practical correlation has been possible between the test and service experience.

With the appreciation that all sewn portions of leather articles in service are subjected to a more or less continuous series of periodic stresses we have developed a test method which in an accelerated fashion simulates the conditions of leather in service or use and may be applicable to any type leather or other materials which must be sewn.

Dynamic Stitch Tear Apparatus

The dynamic stitch tear apparatus as shown in Figure 1 consists of a gear-head motor (A) which turns a cam (B) at 35 revolutions per minute. The stroke of the connecting rod (C) is adjustable on the cam. Through the cam and connecting rod, plate (D) is given a reciprocating motion. Upon the plate are mounted three jaws which hold the specimens (E) under test. Opposite each jaw is another jaw which holds a wire threaded through two holes in the specimen. Each of these latter jaws are attached to a calibrated spring (F) which can be adjusted in tension by the knurled knob and screw (G) protruding from the end of the apparatus. A counter is provided (H) which records the number of strokes. A microswitch is provided which stops the machine when any specimen breaks. This apparatus applies a series of dynamic impulses onto a stitch of wire threaded through a specimen.

Test Method

Samples of leather or other material to be tested are cut from designated areas. Each specimen is 2 x 1 inch and perforated with a $^5/_{32}$ awl so that the centers of two holes are $^1/_4$ inch apart, $^1/_4$ inch from one of the 1 inch edges

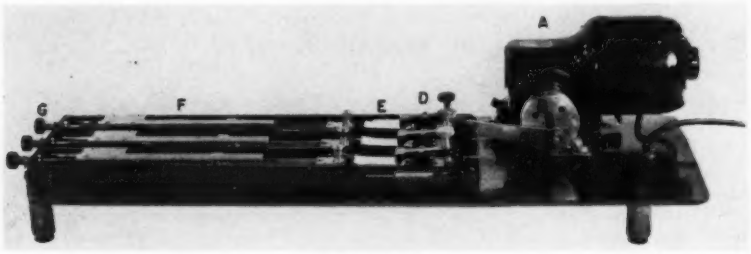

FIGURE 1.

and equidistant from the center line. .040 inch wire, such as found in a No. 1 paper clip, is threaded through the holes so that the wire is pulled through from the finished side. The wire is changed after each test. The specimens can be run in the machine either to failure or to some arbitary value considered a maximum. Initial maximum tension was set at approximately 50 per cent of the average of a determined static stitch tear value and then increased or decreased by 5 pound increments until a tension was established which caused the material to fail. This was done on replicate specimens.

Test Results

In Table I are some results obtained by dynamic test procedure on upholstery leather.

It is shown that the correlation between static stitch tear value and dynamic stitch tear is good but no direct mathematical relationship was established. It is shown that even though static stitch tear values are high for some individual specimens the dynamic fatigue values tend to level off at a much lower value. Also it is shown that specimens with low static values on the whole would withstand 5000 cycles of continuous impulses at greater than half the static value. When leathers are tested at a stress near their static value they fail rapidly, but as we approach a value near equal to one half of their static value we see that the dynamic life of the sample is greatly lengthened.

Table II shows a set of data for some of the better imitation leather materials. Here it is shown that a great variation exists between the two directions of weave of a supported film type material. It can be seen that the unsupported films are almost completely lacking in stitch tear fatigue resistance, no matter what the thickness. Apparently the plastic coating had very little effect on the tear resistance of any of the materials tested. The transportation grade imitation leather upholstery material tested had an extremely heavy plastic coating applied to the fabric yet the tear fatigue resistance was little better than the heavy grade which has a finish coat which is $^2/_3$ the

TABLE I

Dynamic Stitch Tear Fatigue of Some Upholstery Leathers

	Thickness inches	Static stitch tear, lbs.	Number of cycles to break at maximum tension of ——— pounds 15	20	25	30	35	40	45	50
Corrected top grain upholstery leather	.058	39	—	—	15000+	1920	—	—	—	—
	.049	23	10000+	820	—	—	—	—	—	—
	.051	45	—	—	10000+	8080	1240	—	—	—
	.051	20	2830	—	—	—	—	—	—	—
	.058	54	—	—	—	—	10000+	1700	—	—
Deep buff upholstery leather	.053	67	—	—	—	10000+	—	810	475	—
	.040	26	—	9	—	—	—	—	—	—
	.049	65	—	—	—	—	10000+	1440	760	—
	.049	56	—	—	—	10000+	—	130	70	—
	.053	52	—	—	—	10000+	1080	750	—	—
	.070	90	—	—	—	—	—	—	—	10000+

thickness of the transport grade. It is seen that the dynamic stitch tear resistance of these materials decreases rapidly with the first few impulses and then levels off to a more gradual decrease in strength with time at approximately $^1/_2$ the static value.

Theoretical Considerations

As a possible explanation of the short dynamic life of samples at stresses near their static value we can postulate: Due to the fiber architecture which accounts for the inherent strength, and which may be disoriented by dynamic influence, the fibers in the area of dynamic stress are individually broken at the high stresses, but when the stress is reduced to about half of the respective samples static value the fibers are not ruptured but merely compressed in the are of the test and remain collectively strong enough to withstand a large number of impulses in the tester.

In the case of the imitation materials the picture is probably similar at least for fabric reinforced material. The solid plastic films have no fibrous structure to prevent tearing and depend upon cohesive forces which are at best rather low against tearing action, thus the dynamic tear resistance of plastic films is negligible.

TABLE II

Dynamic Stitch Tear Fatigue of Some Imitation Leather Upholstery Materials.

Direction of weave*	Thickness inches	Static stitch tear, lbs.	Number of cycles to break at maximum tension of ——pounds 5	10	15	20	25	30	35	40	45
A-perpendicular	.026	36	—	—	—	10000+	400	5	—	—	—
A-parallel	.026	38	—	—	10000+	4360	44	8	—	—	—
B-perpendicular	.028	38	—	—	10000+	4600	115	130	—	—	—
B-parallel	.028	43	—	—	—	10000+	7800	990	60	—	—
C-perpendicular	.030	36	—	—	—	10000+	650	110	—	—	—
C-parallel	.030	50	—	—	—	—	10000+	4000	250	—	—
D-perpendicular	.044	36	—	—	—	10000+	4460	17	3	—	—
D-parallel	.044	50	—	—	—	—	—	10000+	4280	8	—
E-perpendicular	.023	17	—	820	2	—	—	—	—	—	—
E-parallel	.023	22	—	10000+	11	—	—	—	—	—	—
F-perpendicular	.020	6	20	—	—	—	—	—	—	—	—
F-parallel	.020	5	1	—	—	—	—	—	—	—	—
G-perpendicular	.041	48	—	—	—	10000+	—	830	26	8	—
G-parallel	.042	51	—	—	—	—	10000+	6240	81	47	5
H-perpendicular	.025	41	—	—	—	—	10000+	5140	2	—	—
H-parallel	.025	41	—	—	—	10000+	1830	20	4	—	—
I-perpendicular	.034	40	—	—	10000+	1920	32	18	—	—	—
I-parallel	.034	48	—	—	—	10000+	170	240	5	—	—
J-perpendicular	.029	38	—	—	—	10000+	3550	24	3	—	—
J-parallel	.029	44	—	—	—	10000+	8840	580	34	—	—
K-perpendicular	.028	6	25	—	—	—	—	—	—	—	—
K-parallel	.028	7	75	—	—	—	—	—	—	—	—
L-perpendicular	.034	8	10	—	—	—	—	—	—	—	—
L-parallel	.034	22	—	2800	270	—	—	—	—	—	—

*For unsupported film material this is the direction of the material in the roll. For the Plastic coated fabrics it is the direction of the weave of the fabric reinforcement.

As a summation of the properties of upholstery fabrics the following is an estimate of the average dynamic stitch tear resistance for these materials—

1. Top grain or snuffed top grain upholstery leather
   3 ounce in thickness (1 ounce equals $^1/_{64}$ inch)
   10,000 cylcles at 25 pounds tension
2. Deep buff upholstery leather
   3 ounce in thickness
   10,000 cycles at 30 pounds tension
3. Transportation grade leather upholstery
   10,000 cycles at 50 pounds tension
4. Unsupported films
   0.020 inch thickness
   Under 25 cycles at 5 pounds tension
5. Plastic coated fabric
   .020 to .025 inch thickness
   Under 10,000 cycles at 10 pounds

6. Plastic coated fabric heavy grade
   0.023 to .032 inch thickness
   Under 10,000 cycles at 25 pounds in one or both directions of weave.
7. Plastic coated fabric transport grade
   0.040 to .045 inch thickness
   Under 10,000 cycles at 30 pounds in one direction of weave.

The following requirement has been proposed as an inclusion in the Industry Specification for Upholstery Leather—using the method described in this paper:

REQUIREMENT: Leathers shall withstand 5,000 cycles of a continuous alternating load of 0 pounds to a maximum specified load. Loads shall be as follows:

Thickness	Top Grain Snuffed or Corrected	Machine Buff	Deep Buff
.044 to .051 inch (3 oz.)	15	24	30
.052 to .058 inch (3½ oz.)	18	28	35
.059 to .066 inch (4 oz.)	20	32	40
.067 to .075 inch (4½ oz.)	23	36	45

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BOOK NOTICE

Phenomena, Atoms and Molecules. By Irving Langmuir. Philosophical Library, Inc., 15 East 40th Street, New York 16, N. Y. xi+436 pages. 1950. Price $10.00.

In this volume the author presents a collection of twenty papers in eighteen chapters, approximately one-tenth of the number that he has published since 1909.

The first three chapters (31 pages) are of a less scientific nature but deal with the philosophy of science, incentives motivating scientific work, legislative proposals for the promotion of science, and a discussion on the world control of atomic energy. Some of his viewpoints were written shortly after he attended the meeting of the 220th anniversary of the founding of the Academy of Sciences of the U.S.S.R. in Moscow in 1945.

The remaining portion contains chapters on surface chemistry, constitution of liquids, distribution and orientation of molecules, atomic hydrogen, dissociation of hydrogen into atoms, forces near the surfaces of molecules, isomorphism, isoterism and covalence, effects of molecular dissymmetry on properties of matter, metastable atoms and electrons. condensation and evaporation of gas molecules, evaporation, condensation and reflection of molecules and the mechanism of adsorption, evaporation of atoms, ions and electrons from caesium films on tungsten, mobility of caesium atoms adsorbed on tungsten, and types of valence.

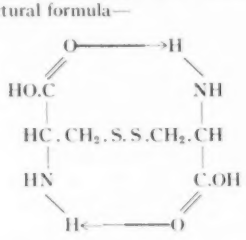
This volume gives the background of fundamental studies which enabled the author to invent the gas-filled tungsten lamp, to isolate atomic hydrogen, to aid in the development of the high vacuum electron tube, and to demonstrate the importance ot chemistry and physics of single layers of atoms and molecules. Much of this material has been the outcome of profiting from experiences, rather than from carefully planned research directed toward specific ends. A bibliography at the end of the book contains a nearly complete list of the author's papers arranged in eight groups.

The timeliness and importance of the principles covered in this volume should prove of value to the scientist interested in advanced physicochemical phenomena.

G.A.R.

ABSTRACTS

Anomalous Rotatory Power of Cystine. By L. F. Fieser, *Rec. Trav. Chim.*, **69,** 410(1950). Through *J. Soc. Dyers and Colourists*, **66,** 338(1950). To explain the remarkably high optical rotatory power of cystine, $[a]_D$ −214°, cited originally by van't Hoff, the author has proposed the structural formula—



based on the Mirsky and Pauling postulate [*Proc. Nat. Acad. Sci.*, **22,** 439(1936)] for the structure and properties of native proteins.

Reaction of Oxidizing Agents with Wool. I. Division of Cystine into Two Fractions of Widely Differing Reactivities. By P. Alexander, R. F. Hudson and M. Fox. *Biochem. J.*, **46,** 27(1950). Through *J. Soc. Dyers and Colourists*, **66,** 454(1950). When wool is treated with hypochlorite solutions at pH 2, 4, and 6 and 25°C., the cystine is almost completely oxidized. at pH 10 only 25–30 per cent of the cystine is oxidized even at 80°C., the excess chlorine being used up in non-cystine reactions. It appears that both free chlorine and hypochlorous acid can oxidize the cystine completely, whereas the hypochlorite ion can oxidize only 25 per cent. The portion of the cystine which is oxidized by the hypochlorite ion is the first portion to react during acid chlorination. Acid permanganate oxidizes only the same portion as this hypochlorite ion. Peracetic acid oxidizes all the cystine, but the last 25 per cent is oxidized only slowly. The difference in reactivity of the two cystine fractions cannot be ascribed to morphological causes, since the cystine of physically modified wools and powdered horn shows the same division. The two fractions are not related to the Phillips fractions.

The Disposal of Tannery Wastes. By Thomas R. Camp. Presented at New England Industrial Waste Conference, Cambridge, Mass., June 26 – 28, 1950.

In comparison with domestic sewage, tannery wastes are considered very strong. The spent lime, sodium sulfide, sulfuric acid and tan liquors are the principal constituents that complicate the method of disposal. A representative tannery produces about

800 gallons of waste per hundred pounds of hide processed, the waste averaging 7200 ppm and 2400 ppm, respectively, in total and suspended solids, and has a 5 day B.O.D. content of 1200 ppm. The large amounts of lime used in a tannery result in a pH value generally in excess of 11, and an alkalinity from 2000–3000 ppm.

The spent tan liquors are the source of most of the color. If discharged to a stream containing iron, pyrogallol tannins will cause formation of an inky blue precipitate, while catechol tannins will produce a dark green precipitate. Free sulfide in reaction with iron will result in a black precipitate of ferric sulfide. Known treatment methods are ineffective in reduction of color due to tannins; many tanneries separate the tan liquors from the rest of the wastes and evaporate them for recovery of a marketable by-product.

The type and degree of treatment required for a particular tannery are dependent upon local stream requirements, availability of land, and other related factors. Screening to remove fleshings, hair and hide shavings is an essential part of a satisfactory disposal system. Mechanically cleaned bar racks with openings of $\frac{3}{8}$ to $\frac{1}{2}$ inch may be used for this purpose. Removal of suspended and dissolved organic matter by sedimentation without adjustment of pH value is effective. Biological treatment of settled effluent or sludge, however, requires a pH below 9.0 but results in conversion of ionized sulfides to hydrogen sulfide gas unless the soluble sulfides are removed prior to pH reduction. Adequate sedimentation usually suffices to precipitate the sulfides as calcium sulfide, removals of 96 per cent having been obtained in several plants.

Discharge of untreated tannery wastes to municipal sewers frequently results in formation of calcium carbonate which may rapidly clog the sewers. Sedimentation of the wastes, followed by carbonation with flue gas or carbon dioxide, with secondary sedimentation to remove the carbonate, will avoid this difficulty. Where the tannery wastes are to be treated with domestic sewage, it is desirable that the pH of the wastes be lowered by carbonation sufficiently to prevent interference with the biological processes.

The sludge obtained from sedimentation of tannery wastes constitutes a major problem of disposal. Volume amounts to about 10 per cent of the raw waste flow and solid content ranges from 2 per cent to 5 per cent. Storage in open lagoons is an economical solution where adequate land is available. Dewatering, which is accomplished by evaporation and consolidation, can be facilitated by decantation of supernatant liquor. Underdrained sand beds are ineffective due to rapid sealing of the pores of the sand. Partial dewatering by centrifuges or vacuum filters is practical. The former procedure necessitates recirculation of the liquid containing the lighter solids, increasing the sludge volume to be handled. Vacuum filtration requires use of filter aids in order to produce a cake which can be removed easily.

Every problem in tannery waste disposal must be individually studied. In most cases, adequate treatment can be developed but the cost frequently is high. Prospects of reducing the cost of treatment through reclamation of by-products are not encouraging and tanners should endeavor to improve their process so that the wastes can be reduced in volume and objectionable characteristics. H.T.R.

Folin Colorimetric Procedure for Amino Acids. By W. H. Furman, G. H. Morrison and A. F. Wagner. *Anal. Chem.*, **22**, 1561 (1950). The Englis and Fiess modification of the Folin method for the estimation of amino acids does not appear to be adequate for mixtures of various types of these acids. The disparity of the extinction-concentration curves for amino acids is attributed to inductive effects of the various radicals of the different amino acids, and in case of the basic amino acids, to the participation of groups other than the alpha-amino group in the formation of colored complexes. The method is accelerate as applied to many individual amino acids and should be useful with effective separation procedures.

Italian Tanning Machinery Developments. *Lea. Tr. Rev.*, **98,** 215 (1950). A number of new machines are described and illustrated, such as band knife neck-splitting machine, band knife splitting machine, sammy and shaving machines.

Grain Cracks in Hides. By J. R. Furlong. *Colonial Plant and Animal Products*, **1,** No. 2, 143 (1950). Nigerian hides are often received in so badly grain cracked condition that they are practically worthless for upper leather. Experiments were therefore carried out to determine the cause of the damage. Hides were (1) excessively stretched over frames and dried in the open at about 78°F; (2) excessively stretched over poles and dried in like manner; and (3) dried over frames with normal tension. No cracked grain was observed, hence the conclusion was reached that excessive stretching is not the cause of the trouble.

A second test was made wherein hides were spread on the ground in crumpled condition to dry, without pegging. The dry crumpled hides were transferred to the arsenication tanks, treated for 15 hours, then suspended on frames and dried in the sun. There was no folding of the stock. In the second experiment the hides were dried in a crumpled state but subsequently folded severely. The third experiment consisted of arsenicating the green hides immediately after flaying and suspension-dried in the sun. They were folded only once after drying. The tests showed that drying on the ground in a crumpled condition produced grain cracking, and severe folding increased the damage. It is recommended that hides be frame dried and, before the process is completed, the hides be removed and folded but once along the back.

The Drying of Goat Skins. By J. R. Furlong. *Colonial Plant and Animal Products*, **1,** No. 2 147 (1950). Goat skins, when hung flesh out over a thin wire, were dried in sun and shade without damage or noticeable difference in the leather produced from them.

Plastic or Resin Finish. *Lea. Trades Rev.*, **98,** 477 (1950). One of the first plastics to be used in the finishing of side or upper leather was an aqueous emulsion of an acrylic resin, which was applied to snuffed grain as a bottom before the cellulose lacquer finish. It prevented the lacquer from sinking into the leather. Later, fast coating bottom plastic proved invaluable in the finishing of kip sides, semichrome and full chrome sides which were to be treated with a cellulose lacquer.

One of the latest acrylate resin emulsions being used is of the following formula: 24 parts polyethylacrylate, 6 parts ammonium polymethycrylate, 50 parts methanol, and 20 parts of water. Other acrylate resins are on the market which are stated to vary in their flexibility, some being soft, others hard, and some intermediate. Another resin finish is capable of mixture with pigment and wax binder for application on dyed splits–, producing an excellent appearing grain when the splits are dry and printed. Another propôsal is to use concentrated pigment paste-resin mixture containing a small amount of casein to give improved adhesion, flexibility and leveling. Soft plastic finishes are excellent for base coat on splits, as they are more stretchy, fill in the surface and provide a maximum filling effect.

The Standardization of Volumetric Solutions. By Analytical Chemists Committees of Imperial Chemical Industries. *Analyst*, **75,** 577 (1950). The standardization system is based on pure electrolytic silver as ultimate standard, with iodine, sodium carbonate and sodium chloride as working standards and arsenious oxide and potassium dichromate as secondary working standards. The preparation and standardization of each analytical solution is given in detail.

Water Analysis. By S. K. Love, *Analyt. Chem.*, **22,** 264 (1950). This is a review of analytical methods that have been applied to the analysis of water and reported in the technical literature during the past year. One hundred nine references are cited.

Kjeldahl Method for Nitrogen. By P. L. Kirk. *Analyt. Chem.*, **22,** 355 (1950). The most important unsolved problems of the Kjeldahl method for total nitrogen are concerned with digestion conditions. The quantity of sulfuric acid used in comparison to the size of sample, and the amount of added salt, are factors of importance. Addition of extra sulfuric acid during digestion is often desirable. Mercury is the most effective catalyst for digestion of proteins and usually cannot be satisfactorily replaced by selenium, which must be kept under constant control. Oxidizing agents, except hydrogen peroxide, should be used with greatest care. Length of digestion after clearing requires further attention. The milligram scale Kjeldahl method is recommended for general application. The ultra micromethod, in which the ammonia is separated by diffusion, is convenient and suitable for many small scale uses. Significant developments in reducing the size of sample into the submicrogram range are to be expected, through the use of the spectrophotometer equipped with capillary cells, and improvements in spectrophotometric instrumentation.

A Permanent Marking Ink for Porcelain Ware. By M. W. Greene, *Chemist Analyst*, **39,** 90 (1950). One gram of potassium carbonate, 1 gram of borax, 2 grams of litharge and 2 grams of cobalt nitrate crystals (dried at 100° for 1 hour) are ground together in a mortar to a fine powder. To the powder, 5 or 6 drops of glycerine are added with continued grinding and then water a few drops at a time until the suspension is of suitable consistency to flow from a pen. After marking the porcelain with the ink, the vessel is heated to redness for 1–2 minutes over an oxidizing flame. On cooling, a blue numeral fused in the porcelain will appear.

Peptides of Cystine in Partial Hydrolysates of Wool. By R. Consden and A. H. Gordon. *Biochem. J.*, **46,** 8 (1950). Through *J. Soc. Dyers and Colourists*, **66,** 454 (1950). Thirteen dipeptides of cystine in partial hydrolysates of wool have been separated and identified by means of two-dimensional chromatography on paper. It is concluded that, in wool, most of the monoamino-monocarboxylic acids are combined through both their amino and carboxyl groups to cystine residues. Evidence for the formation of intermediate oxidation products of combined cystine by the action of hydrogen peroxide has been obtained.

Chromatographic Methods in Amino Acid Analysis. By R. L. M. Synge. *Chem. and Ind.* Aug. 18, 339 (1950). In chromatographic work the three main operational procedures are: (1) frontal analysis, where the original mixed solution is passed continuously through the column, (2) election development, where the original mixed solution is placed on the column in small volume and washed through with pure solvent, (3) displacement development, where the original mixed solution is placed on the column in small volume and washed through with a solution of some displacing agent; (4) development with change of solvent, where, after placing the original mixed solution on the column, different solvent mixtures, acting as eluting or displacing agents, are successively passed through the chromatographic column. The behavior of substances on a chromatographic column depends primarily on their distribution equilibria between the moving and stationary phases of the chromatogram. This distribution may be determined by various types of mechanism. Those considered responsible for separation of amino acids can be classified as dependent on (a) molecular adsorption, (b) ion-exchange adsorption, (c) partition between liquid phases. All three have proved useful in separation of amino acids. Analytical purposes to

which some of the chromatographic methods may be put are (a) two dimensional chromatography on paper for the qualitative determination of proteins in small quantities, (b) partition chromatography on columns of starch or cellulose for accurate, quantitative work on proteins, (c) chromatograph on sulfonated polysterene resin for amino acid separation of different sequence than the starch column, (d) ultramicroscope isotope dilution analysis for amino acids in minute quantities, (e) systematic group separations of amino acids by adsorption on charcoal and ion-exchanges, and (f) end group assay wherein the free amino groups of proteins are substituted with fluorodinitrobenzene, hydrolyzing the resulting *N*-dinitrophenyl derivatives to give *N*-dinitrophenyl amino acids, and separating these by chromatography on moist silica gel with organic solvents. This method is useful in identifying free amino groups of proteins.

Intramolecular Rotation and the Structure of High Polymers. I. The Structure of Polypeptide Chain. By T. Simanonti and S. Mizuschima. *Bul. Chem. Soc. Japan*, **21,** 1(1948). In addition to the stable extended form of the polypeptide chain, corresponding to the structure of silk fibroin and β-keratin, the authors propose a second stable chain configuration characterized by the existence of intramolecular hydrogen bond. Diagramatic structure are shown for the cystine bond in α– and β–keratin, and contracted wool.

The Use of Tannin in the Estimation of Zirconium and Its Separation from Thorium. B. A. Purushottam and B.S.V.R.Rao. *Analyst*, **75,** 555 (1950). Zirconium is quantitatively precipitated by tannin from a chloride solution up to 0.15 *N* in hydrochloric acid. By double precipitation at this acidity it can be quantitatively separated from thorium.

The Micro Kjeldahl Determination of Serum Proteins with Selenium and Copper as Catalysts. By B. Levin, V. G. Oberholzer and T. P. Whitehead. *Analyst.* **75,** 561 (1950). The authors determined that the optimum for 0.1 ml. of serum are 3.5 mg. of selenium 20 mg. of copper sulfate, 1.0 gr. of sodium sulfate and 1.0 ml. of sulfuric acid for a digestion time of one hour.

Recovery of Grease from Wool Scouring Waste and Abatement of Stream Pollution through Calcium Hypochlorite Process. By A. A. Cameron. *Dyestuffs Reporter*, **39,** 667 (1950). Wool scouring water is treated with 6-7 per cent by volume of calcium hypochlorite, the sludge settled, supernatant water decanted, the grease filtered and recovered as a good grade of degras. Several factors govern the economics of the process.

PATENTS

Adhesive. B. P. 636,423. B. J. Balfe. An adhesive suitable for bonding fabrics, leather and the like is prepared by dissolving in a solvent, such as acetone, a modified polyesteramide as described in B. P. 580,524 and a resin prepared by condensing phenol or a phenolic resin with terpene.

Waterproofing Leather. B. P. 637,095. C. G. Shaw, Leather is waterproofed without loss of resilience by impregnation with a molten water proofing substance, such as fat, grease or wax, which is normally brittle and of melting point not less than 50°C., excess being removed by wetting the grain and flesh sides with an aqueous detergent above the wax melting point, which swells the leather fiber and thus expresses the wax, the residue being hardened by quick cooling.

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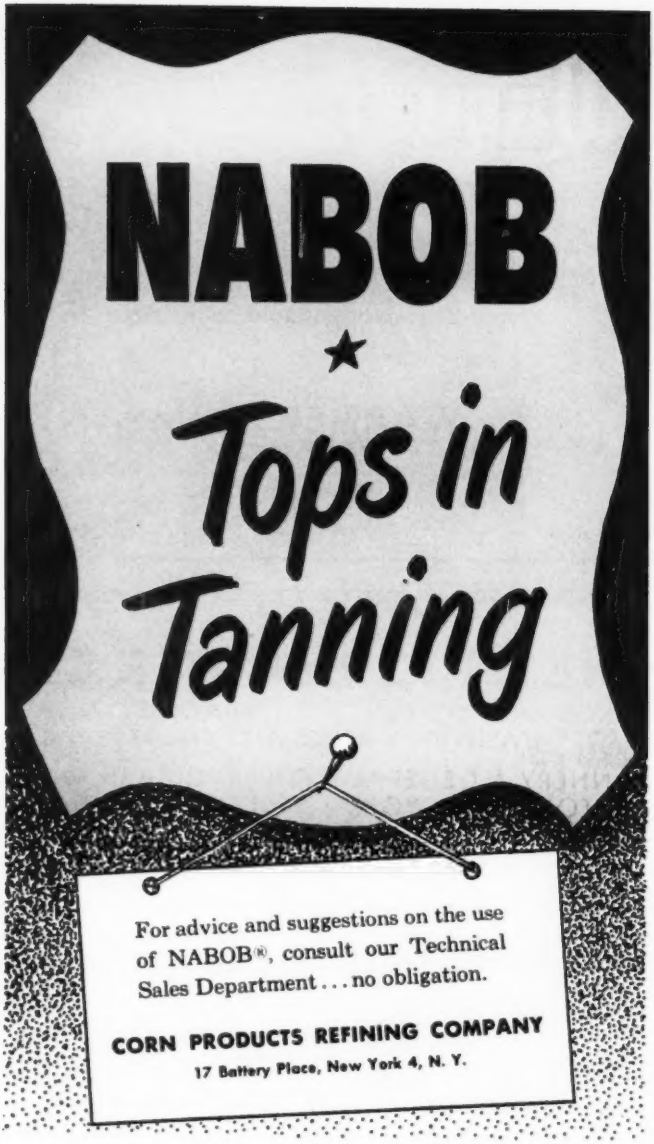
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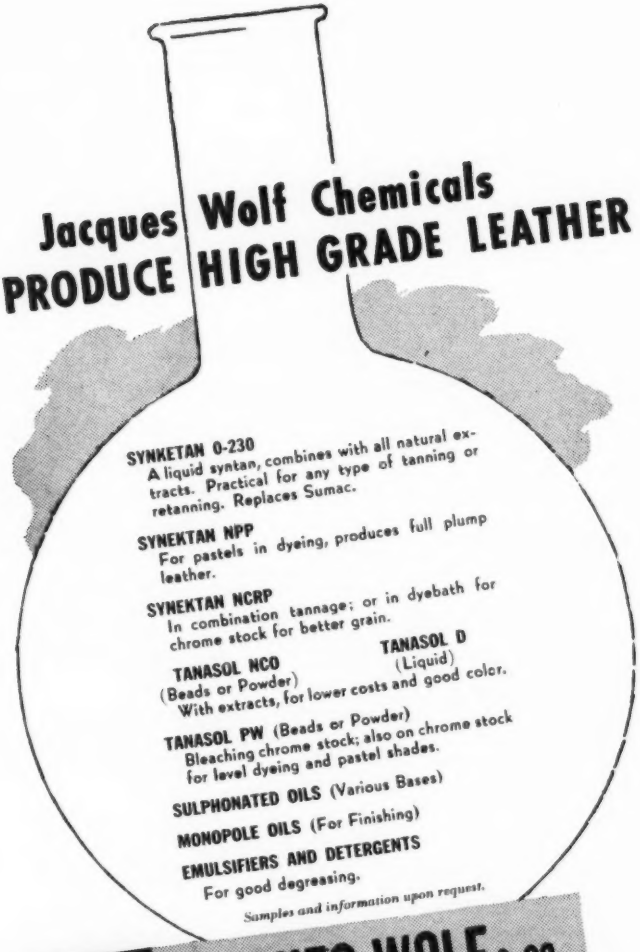

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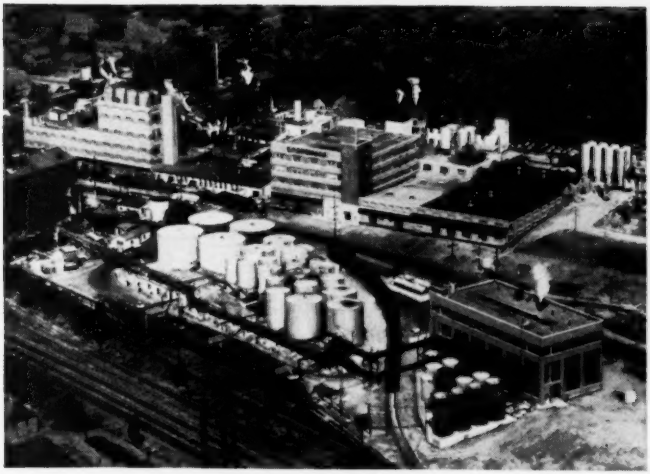

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